

# PATENT ABSTRACTS OF JAPAN

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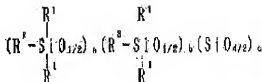
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## (54) CURABLE RESIN COMPOSITION

(57)Abstract:

**PURPOSE:** To obtain the composition, excellent in fluidity before curing and flexibility and adhesion after the curing and useful as a sealing resin for electrical and electronic elements by blending a curable resin with a specific organopolysiloxane.

**CONSTITUTION:** This curable resin composition comprises (A) 100 pts.wt. curable resin and (B) 0.1-500 pts.wt. organopolysiloxane, expressed by the formula {R<sup>1</sup> is a ≤5C alkyl or phenyl; R<sup>2</sup> is a ≤5C alkyl, phenyl or H; R<sup>3</sup> is an epoxy group-containing organic group, an alkoxysilylalkyl or a ≥6C alkyl; (a) is 0 or a positive number; (b) and (c) are positive numbers; (a/c) is 0-4; (b/c) is 0.05-4; [(a+b)/c] is 0.2-4} and having at least one each of the alkoxysilylalkyl group and ≥6C alkyl group in one molecule. Furthermore, the component (A) is preferably selected from the group consisting of an epoxy resin, a phenolic resin, an imide resin and a silicone resin and the component (B) has preferably further an epoxy group-containing organic group.





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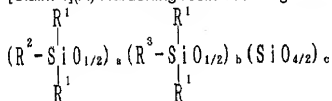
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**CLAIMS**


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[Claim(s)]

[Claim 1](A) Hardening resin 100 weight section and the (B) general formula : [Formula 1]



(R<sup>1</sup> is a with a carbon number of five or less low-grade alkyl group or a phenyl group among a formula, R<sup>2</sup> is a basis chosen from the group which consists of a with a carbon number of five or less low-grade alkyl group, a phenyl group, and a hydrogen atom, and R<sup>3</sup> is a basis chosen from the group which consists of an epoxy group content organic group, an alkoxy silyl alkyl group, and a with a carbon numbers of six or more alkyl group. a is 0 or a positive number, b is a positive number, c is a positive number, a/c is the number of 0-4, and b/c is the number of 0.05-4, and (a+b)/c is the number of 0.2-4. The hardenability resin composition which consists of 0.1 to organopolysiloxane 500 weight section which is expressed with } and has an alkoxy silyl alkyl group and at least one with a carbon numbers of six or more alkyl group at a time in a monad.

[Claim 2](A) The hardenability resin composition according to claim 1, wherein an ingredient is hardening resin chosen from a group which consists of an epoxy resin, phenol resin, imide resin, and silicone resin.

[Claim 3](B) The hardenability resin composition according to claim 1, wherein an ingredient is organopolysiloxane which has an epoxy group content organic group, an alkoxy silyl alkyl group, and at least one with a carbon numbers of six or more alkyl group at a time in a monad.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application]About a hardenability resin composition, in detail, this invention is excellent in mobility before hardening, and relates to the hardenability resin composition which serves as hardening resin excellent in flexibility and an adhesive property after hardening.

[0002]Since mechanical properties, such as electrical properties, such as the dielectric characteristics of the hardening resin produced by hardening this, volume resistivity, and electrical breakdown strength, or flexural strength, compressive strength, and impact strength, are excellent, the hardenability resin composition is used for the electrical and electric equipment and sealing resin for electronic devices, adhesives, resin for FRP, etc.

[0003]Generally, a hardenability resin composition has the upright hardening resin produced by hardening this, and Since [ lacking in flexibility and ] the rate of cure shrinkage at the time of hardening is large, If this is used as the electrical and electric equipment and sealing resin for electronic devices, in order to add big stress to the electrical and electric equipment and an electronic device, There was a problem of producing a crack in hardening resin itself, or destroying the electrical and electric equipment and an electronic device, or producing a crevice between the electrical and electric equipment and an electronic device, and hardening resin since the adhesive property over the electrical and electric equipment and electronic device of hardening resin is still lower. The coefficient of thermal expansion of the hardening resin produced by hardening this a hardenability resin composition to the coefficient of thermal expansion of the electrical and electric equipment and an electronic device Since it is large, If the resin seal electrical and electric equipment and an electronic device receive a thermo cycle, in order to add big stress to the electrical and electric equipment and an electronic device, There was a problem of producing a crack in hardening resin itself, or destroying the electrical and electric equipment and an electronic device, or producing a crevice between the

electrical and electric equipment and an electronic device, and hardening resin since the adhesive property over the electrical and electric equipment and electronic device of hardening resin is still lower. When water moreover invaded into the crevice between the crack or hardening resin produced by the cure shrinkage of a hardenability resin composition, or thermal expansion contraction, and the electrical and electric equipment and an electronic device, there was a problem of promoting degradation of the resin seal electrical and electric equipment and an electronic device.

[0004] Thus, in the hardenability resin composition, in order to low-stress-ize hardening resin, the flexibility of hardening resin is raised, and the hardenability resin composition of the versatility which makes the adhesive property over the electrical and electric equipment and electronic device of hardening resin come to improve is proposed. For example, an epoxy resin, a methylphenyl polysiloxane, the organopolysiloxane that consists of bifunctional siloxane units (D unit) which have an epoxy group, and trifunctional siloxane units (T unit), The hardenability resin composition which consists of an inorganic filler and a catalyst for hardening (refer to JP,56-145942,A), . Have an epoxy resin, an epoxy group or an amino group and a hydroxyl group, or at least one basis that can be hydrolyzed, respectively. The organopolysiloxane which consists of monofunctional siloxane units (M unit) or trifunctional siloxane units (T unit), and bifunctional siloxane units (D unit), The hardenability resin composition which consists of a hardening agent and an inorganic filler (refer to JP,56-136816,A), An epoxy resin, phenol resin, the hardenability resin composition that becomes a chain side chain from the dimethylpolysiloxane which has an epoxy group and a polyoxyalkylene group (refer to JP,60-58425,A), And the hardenability resin composition (refer to JP,64-51467,A) which consists of hardening resin and silicone rubber spherical pulverized coal is proposed.

[0005] However, the hardenability resin composition proposed by JP,56-145942,A and JP,56-136816,A, Since the organopolysiloxane which makes bifunctional siloxane units (D unit) indispensable is used, There was a fault that the glass transition point (Tg) of the obtained hardening resin fell, and it was remarkable especially when using Loki Sun for the organopolysiloxane which consists of  $2\text{SiO}_2/a\text{2}$  unit (D unit) which has an epoxy group ( $\text{CH}_3$ ).

The hardenability resin composition proposed by JP,60-58425,A, In order to use the dimethylpolysiloxane which has an epoxy group and a polyoxyalkylene group for a chain side chain, there was a fault that the obtained hardening resin had large absorptivity and it was not suitable as the electrical and electric equipment and sealing resin for electronic devices. The hardenability resin composition proposed by JP,64-51467,A, Although the flexibility of the hardening resin produced by hardening this was excellent, since the mobility of a hardenability resin composition was bad, there was a fault that the workability which carries out the resin seal of the electrical and electric equipment and the electronic device was bad, and this

hardening resin had a still worse adhesive property over the electrical and electric equipment and an electronic device.

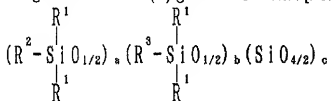
[0006]

[Problem(s) to be Solved by the Invention] This invention persons reached this invention, as a result of trying hard wholeheartedly, in order to solve the above-mentioned problem.

[0007] That is, the purpose of this invention is to provide the hardenability resin composition used as the hardening resin in which mobility was excellent in before hardening and flexibility and an adhesive property were excellent after hardening.

[0008]

[The means for solving a problem, and its operation] This invention is (A) hardening resin. 100 weight section and (B) general formula : [Formula 2]



{R<sup>1</sup> is a with a carbon number of five or less low-grade alkyl group or a phenyl group among a formula, R<sup>2</sup> is a basis chosen from the group which consists of a with a carbon number of five or less low-grade alkyl group, a phenyl group, and a hydrogen atom, and R<sup>3</sup> is a basis chosen from the group which consists of an epoxy group content organic group, an alkoxy silyl alkyl group, and a with a carbon numbers of six or more alkyl group. a is 0 or a positive number, b is a positive number, c is a positive number, a/c is the number of 0-4, and b/c is the number of 0.05-4, and (a+b)/c is the number of 0.2-4. It is expressed with} and related with the hardenability resin composition which consists of 0.1 to organopolysiloxane 500 weight section which has an alkoxy silyl alkyl group and at least one with a carbon numbers of six or more alkyl group at a time in a monad.

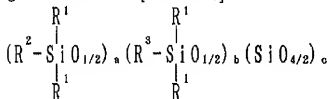
[0009] The hardenability resin composition of this invention is explained in detail.

[0010] (A) Hardening resin is a substrate of this invention. (A) Conventionally, especially if an ingredient is publicly known hardening resin, it will not be limited. (A) As an ingredient specifically, Phenol resin, formaldehyde resins, xylene resin, xylene-formaldehyde resin, ketone formaldehyde resins, furan resin, urea resin, imide resin, melamine resin, an alkyl resin, unsaturated polyester resin, aniline resin, sulfone amide resin, Silicone resin, epoxy resins, and these copolymer resin are illustrated, and the hardening resin of the above-mentioned illustration can also be used combining two or more sorts. In the hardening resin of these illustration, it is hardening resin especially chosen from the group which consists of an epoxy resin, phenol resin, imide resin, and silicone resin preferably as a (A) ingredient. The hardening resin hardened with high energy beams which the curing means in particular of the

(A) ingredient is not limited, for example, are hardened with heat, such as hardening resin, ultraviolet rays, or radiation, and the hardening resin hardened with humidity are mentioned. The (A) ingredient is liquefied at a room temperature, or it may be hardening resin of which state of a solid state, and it may contain the organic solvent etc.

[0011](A) A hardening agent, a hardening accelerator, a bulking agent, a photosensitizer, higher-fatty-acid metal salt, an ester system wax, a plasticizer, etc. can be blended with an ingredient as ingredients other than the hardening resin of the above-mentioned illustration. (A) As a hardening agent which can be blended with an ingredient specifically, Organic acid, such as carboxylic acid and sulfonic acid, and the anhydride of those, an organic hydroxy compound, a silanol group, The amino compound of the organic silicon compound and the first class which have bases, such as an alkoxy group or a halogeno group, or the second class can be illustrated, and it can also be used, combining these two or more sorts. As a hardening accelerator which can be blended with the (A) ingredient, specifically, Organophosphorus compounds, such as organic metallic compounds, such as the third class amine compound, aluminum, and a zirconium, and phosphine, a different ring type amine compound, a boron complex compound, organic ammonium salt, organic sulfonium salt, organic peroxide, etc. are illustrated. As a bulking agent which can be blended with the (A) ingredient, specifically, Glass fiber, asbestos, an alumina fiber, alumina, and silica. Fibrous fillers, such as the ceramic fiber used as an ingredient, a boron fiber, a zirconia fiber, silicon carbide fiber, a metal fiber, polyester fiber, an aramid fiber, a nylon fiber, a phenol fiber, and natural animals-and-plants textiles, fused silica, precipitation silica, fumed silica, pyrogenic silica, a zinc oxide, Calcination clay, carbon black, a glass bead, alumina, talc, calcium carbonate, clay, aluminium hydroxide, barium sulfate, a titanium dioxide, aluminum nitride, silicon carbide, magnesium oxide, beryllium oxide, kaolin, mica, Particulate matter-like bulking agents and these mixtures, such as zirconia, are illustrated.

[0012](B) Organopolysiloxane is an ingredient for raising the mobility of the hardenability resin composition of this invention, raising the flexibility of the hardening resin produced by hardening this, and raising the adhesive property over adherends, such as metal, and is a general formula. : [Formula 3]



It is organopolysiloxane come out of and expressed.  $R^1$  is a with a carbon number of five or less low-grade alkyl group or a phenyl group among an upper type, and, specifically, a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group are illustrated as a



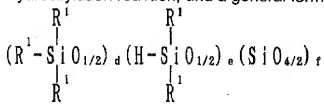
with a carbon number of five or less low-grade alkyl group. Among an upper type,  $R^2$  is a basis chosen from the group which consists of a with a carbon number of five or less low-grade alkyl group, a phenyl group, and a hydrogen atom, and, specifically, a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group are illustrated as a with a carbon number of five or less of  $R^2$  low-grade alkyl group.  $R^3$  is a basis chosen from the group which consists of an epoxy group content organic group, an alkoxy silyl alkyl group, and a with a carbon numbers of six or more alkyl group among an upper type, As an epoxy group content organic group of  $R^3$ , specifically, 2-glycidoxo ethyl group, 3-glycidoxo propyl group, 4-glycidoxobutyl group, 5-glycidoxo pentyl group, 2-(3,4-epoxycyclohexyl) ethyl group, 3-(3,4-epoxycyclohexyl) propyl group, 4-(3,4-epoxycyclohexyl) A butyl group is illustrated and as an alkoxy silyl alkyl group of  $R^3$  specifically, A trimethoxysilyl ethyl group, a trimethoxysilylpropyl group, a trimethoxysilyl butyl group, a trimethoxysilyl pentyl group, a triethoxy silyl ethyl group, a triethoxy silyl propyl group, a triethoxy silyl butyl group, a methyl dimethoxy silyl ethyl group, A methyl dimethoxy silyl propyl group, a dimethyl methoxy silylethyl group, and a dimethyl methoxy silylpropyl group are illustrated, and as a with a carbon numbers of six or more of  $R^3$  alkyl group specifically, A hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, the dodecyl, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, and an octadecyl group are illustrated, n-hexyl group, n-heptyl group, n-octyl group, n-nonyl group, n-decyl group, n-undecyl group, n-dodecyl, n-tridecyl group, n-tetradecyl group, an n-pentadecyl group, n-hexadecyl group, n-heptadecyl group, and n-octadecyl group are preferred. (B) It is required for the carbon number of the alkyl group of  $R^3$  to be six or more in an ingredient, Although the maximum in particular was not limited, when this is blended with the (A) ingredient, (A) As for the carbon number of the alkyl group of  $R^3$ , since the compatibility of an ingredient and the (B) ingredient is good and the flexibility and adhesive property of resin after hardening the hardening resin constituent obtained are good, it is preferred that it is the range of 6-30.

[0013]a is 0 or the positive number which shows the number of the monofunctional siloxane units (M unit) which do not have an epoxy group content organic group, an alkoxy silyl alkyl group, or a with a carbon numbers of six or more alkyl group among an upper type, b is a positive number which shows the number of the monofunctional siloxane units (M unit) which have an epoxy group content organic group, an alkoxy silyl alkyl group, or a with a carbon numbers of six or more alkyl group, c is a positive number which shows the number of tetrafunctional siloxane units (Q unit), each ratio and a/c are the number of the ranges of 0-4, and b/c is the number of the ranges of 0.05-4, and (a+b)/c is the number of the ranges of 0.2-4. This is for the compatibility of the (A) ingredient and the (B) ingredient to fall that

monofunctional siloxane units (M unit) cannot surpass four pieces, but monofunctional siloxane units (M unit) are less than 0.2 piece to one tetrafunctional siloxane units (Q unit). In the hardenability resin composition of this invention, in order for the compatibility of the (A) ingredient and the (B) ingredient to be excellent, (B) It is because the monofunctional siloxane units (M unit) which have an epoxy group content organic group in an ingredient, an alkoxy silyl alkyl group, or a with a carbon numbers of six or more alkyl group need to be at least 0.05 piece to one tetrafunctional siloxane units (Q unit). (B) Although an ingredient is liquefied at a room temperature, or it is a solid state and the molecular weight in particular is not limited, since compatibility with the (A) ingredient is good, it is preferred that it is the range of 500-500,000.

[0014]In the hardenability resin composition of this invention, the (B) ingredient, Since it has an alkoxy silyl alkyl group and a with a carbon numbers of six or more alkyl group, (A) Since the flexibility of the hardening resin obtained by being incorporated into the resin matrix of an ingredient improves and the (B) ingredient consists of a  $\text{SiO}_2$  unit (Q unit), it has the advantage of excelling in flexibility and an adhesive property.

[0015]The above-mentioned (B) ingredients are the bottom of existence of the catalyst for a hydrosilylation reaction, and a general formula, for example. : [Formula 4]



{ $\text{R}^1$  is a with a carbon number of five or less low-grade alkyl group or a phenyl group among a formula. d is 0 or a positive number, e is a positive number, f is a positive number, d/f is the number of 0-4, and e/f is the number of 0.05-4, and (d+e)/f is the number of 0.2-4. It can prepare by making the organopolysiloxane expressed with} carry out the addition reaction of the organic compound which has an epoxy group and aliphatic unsaturated bonds if needed to an alkoxy silylalkene and a with a carbon numbers of six or more alkene.

[0016]In the hardenability resin composition of this invention, the loadings of the (B) ingredient are 0.1 - 500 weight section to (A) ingredient 100 weight section.

It is 0.5 to 100 weight section preferably.

This is for the flexibility of the hardening resin obtained as the loadings of the (B) ingredient are less than 0.1 weight sections to (A) ingredient 100 weight section not to improve.

When this surpasses 500 weight sections, it is for the mechanical strength of the obtained hardening resin to fall remarkably.

[0017]The hardenability resin composition of this invention can be prepared by mixing the (A) ingredient and the (B) ingredient uniformly. (A) The method in particular of mixing an ingredient and the (B) ingredient is not limited, but specifically, (A) After blending and carrying out the premix of the (B) ingredient at the time of the method of blending the (B) ingredient with an ingredient directly, and (A) ingredient preparation, the method of blending additive agents, such as a bulking agent, with the (A) ingredient and the method of blending with the (B) ingredient various kinds of additive agents blended with the (A) ingredient one by one are illustrated. (A) Although there is no limitation and a mixed device is chosen by the gestalt of versatility [ ingredient / the (A) ingredient or / (B) ], such as a liquid, a solid state, and powder, especially as a mixed device which mixes an ingredient and the (B) ingredient, Specifically, the continuous mixer of one axis or two axes, 2 rolls, a loss mixer, and a kneader mixer are illustrated.

[0018]Since mobility is excellent before hardening, the hardenability resin composition of this invention can be used by methods, such as a transfer mold, injection molding, potting, casting, powder coating, dip coating, and dropping. Since after hardening becomes hardening resin excellent in flexibility and an adhesive property, the hardenability resin composition of this invention can be used for the hardenability resin composition for closing the electrical and electric equipment and an electronic device, adhesives, etc.

[0019]

[Example]An example explains the hardenability resin composition of this invention in detail. Among the example, the value of viscosity is a value measured in 25 \*\*, and measured the various characteristics of a hardenability resin composition and hardening resin by the following method.

[0020]O Spiral flow : it measured by the method according to an EMMI standard.

O Molding shrinkage : It measured by the method according to JIS-K-6911.

O Coefficient of thermal expansion : The hardening resin fabricated to 5mmx5mmx16mm was measured using the thermal expansion meter (DL-7000 by a vacuum science-and-engineering company). The value of a coefficient of thermal expansion is a value from a room temperature to a glass transition point.

O Glass transition point (Tg) : it measured by coefficient-of-thermal-expansion measurement.

O Rate of bending flexibility : It measured by the method according to JIS-K-6911.

O Water absorption : After making into the temperature of 121 \*\*, and 100% of humidity the hardening resin fabricated to 2 inch x0.5 inch x0.25 inch and humidifying it for 20 hours, it asked by measuring the weight increment of the hardening resin.

O Barricade : The 20-micrometer-deep slot was used and barricade length was measured.

O Adhesive property : After inserting the hardenability resin composition into 42 alloy board and the copper plate and stiffening this, the adhesive property at the time of removing

hardening resin was judged by O (good) and x (poor).

O Thermal shock resistance : 20 resin seal semiconductor devices (chip size  $36 \text{ mm}^2$ , and package 2.0 mm in thickness) are fabricated, This was performed at  $-196^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ , the heat cycle test was done in the cycle for 1 minute, the sealing resin surface was observed with the stereoscopic microscope after 150 cycles, and the case where they were \*\* and 11 pieces or more about the case where they are O and 6-10 pieces about the case where the number of the mold goods in which the crack went into the surface is five or less pieces was made into x.

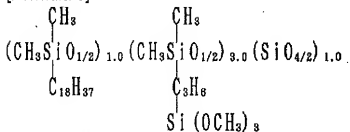
O Solder heat resistance : 20 resin seal semiconductor devices (chip size  $36 \text{ mm}^2$ , and package 2.0 mm in thickness) were fabricated, this was promptly immersed in a  $240^{\circ}\text{C}$  solder bath after 72-hour neglect under 85%RH conditions at  $85^{\circ}\text{C}$  for 1 hour, and the sealing resin surface was observed with the stereoscopic microscope. The case where they were \*\* and 11 pieces or more about the case where they are O and 6-10 pieces about the case where the number of the mold goods in which the crack went into the surface is five or less pieces was made into x.

[0021]

[Reference example 1] making allyl trimethoxysilane and 1-OKUTADEN tetrakis (dimethyl siloxy) Silang react to agitating equipment, a flowing-back condenser tube, and a 4 mouth flask with a thermometer under existence of chloroplatinic acid in toluene -- a yellowish brown color -- transparent organopolysiloxane was prepared. The viscosity of this organopolysiloxane was 24 centipoises and the refractive index was 1.4358. When  $^1\text{H}$ -nuclear-magnetic-resonance-spectrum analysis (following, NMR),  $^{13}\text{C}$ -NMR, and  $^{29}\text{Si}$ -NMR analyzed this organopolysiloxane, what is expressed with the following structural formula was checked.

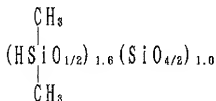
[0022]

[Formula 5]



[0023]

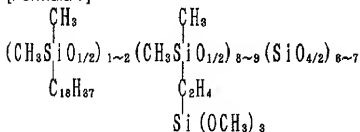
[Reference example 2] It is a formula to agitating equipment, a flowing-back condenser tube, and a 4 mouth flask with a thermometer. : [Formula 6]



Came out, reacted the organopolysiloxane (0.92 % of the weight of content of 46 centipoise viscosity and a silicon atom absorbed water matter atom) expressed in toluene, vinyltrimetoxysilane was made to react to 1-octadecene under existence of a chloroplatinic acid catalyst, and water-white organopolysiloxane was prepared. The viscosity of this organopolysiloxane was 97 centipoises and the refractive index was 1.4386. When  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and  $^{29}\text{Si-NMR}$  analyzed this organopolysiloxane, what is expressed with the following structural formula was checked.

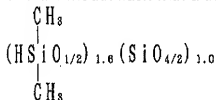
[0024]

[Formula 7]



[0025]

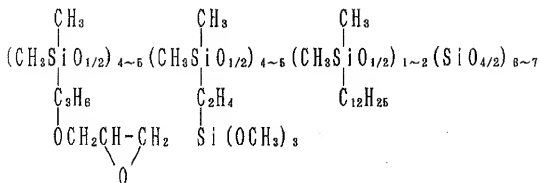
[Reference example 3] It is a formula to agitating equipment, a flowing-back condenser tube, and a 4 mouth flask with a thermometer. : [Formula 8]



Come out and the organopolysiloxane (0.92 % of the weight of content of 46 centipoise viscosity and a silicon atom absorbed water matter atom) expressed in toluene, Allyl glycidyl ether was made to react to 1-dodecen and vinyltrimetoxysilane under existence of a chloroplatinic acid catalyst, and transparent brown organopolysiloxane was prepared. The viscosity of this organopolysiloxane was 142 centipoises and the refractive index was 1.4475. When  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and  $^{29}\text{Si-NMR}$  analyzed this organopolysiloxane, what is expressed with the following structural formula was checked.

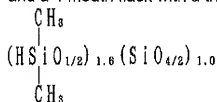
[0026]

[Formula 9]



[0027]

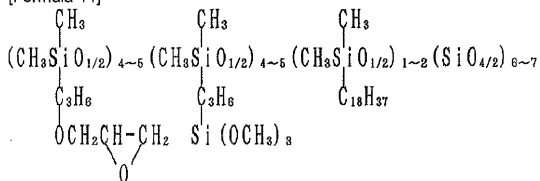
[Reference example 4] It is a formula to agitating equipment, a flowing-back condenser tube, and a 4 mouth flask with a thermometer. : [Formula 10]



Came out, reacted the organopolysiloxane (0.92 % of the weight of content of 46 centipoise viscosity and a silicon atom absorbed water matter atom) expressed in toluene, vinyltrimetoxysilane was made to react to 1-octadecene under existence of chloroplatinic acid, and water-white organopolysiloxane was prepared. The viscosity of \*\*\*\* organopolysiloxane was 97 centipoises and the refractive index was 1.4386. when  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and  $^{29}\text{Si}$ -NMR analyzed this organopolysiloxane, the following structural formula and the thing come out and expressed were checked.

[0028]

[Formula 11]



[0029]

[Work example 1] Phenol novolak resin (80 \*\* of softening temperature, hydroxyl equivalent 100) 100 weight section, Organopolysiloxane 8.9 weight section, fused-quartz powder 185.7 weight section which were prepared by the reference example 1, Hexamethylenetetramine

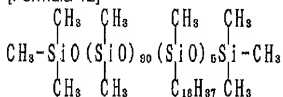
11.4 weight section, 3-glycidoxypolytrimetoxysilane 1.0 weight section, and KARUNA bow wax 2.9 weight section were mixed uniformly, this was further cooled after kneading with a 90 ° heating roller, and the hardenability resin composition of this invention was prepared. Subsequently, this was ground and transfer moulding was carried out for 3 minutes under the conditions of 175 °, and 70 kg / cm<sup>2</sup>. Then, postcure of the hardening resin was carried out over 2 hours at 150 °. The various characteristics of the obtained hardening resin were shown in Table 1.

[0030]

[Comparative example 1] In Example 1, the hardenability resin composition was prepared like Example 1 except having used the organopolysiloxane expressed with a lower type instead of the organopolysiloxane prepared by the reference example 1. This was stiffened like Example 1. The various characteristics of the obtained hardening resin were shown in Table 1.

[0031]

[Formula 12]



[0032]

[Comparative example 2] In Example 1, the hardenability resin composition was prepared like Example 1 except not using the organopolysiloxane prepared by the reference example 1. This was stiffened like Example 1. The various characteristics of the obtained hardening resin were shown in Table 1.

[0033]

[Table 1]

測定項目	本発明	比較例	
	実施例1	比較例1	比較例2
スパイラルフロー (inch)	39	34	31
成形収縮率 (%)	0.23	0.20	0.31
熱膨張率 (×10 <sup>-5</sup> /°C)	1.19	1.05	1.50
ガラス転移点 (°C)	161	138	156
曲げ弾性率 (kgf/mm <sup>2</sup> )	1200	1260	1350
吸水率 (%)	0.39	0.56	0.51

[0034]

[Work example 2]  $\text{CH}_3\text{SiO}_{3/40}$  mol of 2 unit %, and  $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiO}_2/10$  mol of 2 unit %, It consists of  $\text{C}_6\text{H}_5\text{SiO}_{3/40}$  mol of 2 unit %, and  $(\text{C}_6\text{H}_5)_2\text{SiO}_2/10$  mol of 2 unit %, Silicone resin 50 weight section and cresol novolak epoxy resin (80 \*\* of softening temperatures) which contain a silicon atom absorbed water acid radical 5% of the weight Silicone epoxy resin 100 weight section which consists of weight per epoxy equivalent 220 50 weight section, Organopolysiloxane 8.0 weight section, fused-quartz powder 284.6 weight section which were prepared by the reference example 2, Aluminum acetylacetonate 3.5 weight section, 3-glycidioxypropyltrimetoxysilane 1.0 weight section, and KARUNA bow wax 3.8 weight section were mixed uniformly, this was further cooled after kneading with a 90 \*\* heating roller, and the hardenability resin composition of this invention was prepared. Subsequently, this was ground and transfermold shaping was carried out for 2 minutes under the conditions of 175 \*\*, and 70  $\text{kg} / \text{cm}^2$ . Then, postcure of this hardening resin was carried out over 12 hours at 180 \*\*. The various characteristics of the obtained hardening resin were shown in Table 2.

[0035]

[Work example 3] In Example 2, the hardenability resin composition was prepared like Example 2 except having used the organopolysiloxane prepared by the reference example 3 instead of the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 2. The various characteristics of the obtained hardening resin were shown in Table 2.

[0036]

[Work example 4] In Example 2, the hardenability resin composition was prepared like Example 2 except having used the organopolysiloxane prepared by the reference example 4 instead of the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 2. The various characteristics of the obtained hardening resin were shown in Table 2.

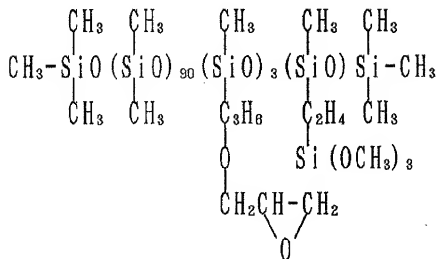
[0037]

[Comparative example 3] In Example 2, the hardenability resin composition was prepared like Example 2 except having used the organopolysiloxane expressed with the following structural formula instead of the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 2. The various characteristics of the obtained hardening resin were shown in Table 2.

[0038]

[Formula 13]





[0039]

[Comparative example 4] In Example 2, the hardenability resin composition was prepared like Example 2 except not adding the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 2. The various characteristics of the obtained hardening resin were shown in Table 2.

[0040]

[Table 2]

測定項目	本 発 明			比 較 例	
	実施例2	実施例3	実施例4	比較例3	比較例4
スバイラルフロー (インチ)	45	44	42	40	35
熱膨張率 ( $\times 10^{-6}/^{\circ}\text{C}$ )	2.26	2.18	2.15	2.90	2.75
曲げ弾性率 ( $\text{kgf}/\text{mm}^2$ )	1110	1090	1150	1250	1520
吸水率 (%)	0.40	0.39	0.38	0.56	0.47
バリ (mm)	3	5	4	15	4
接着性	○	○	○	△	×
耐熱衝撃性	○	○	○	△	×
半田耐熱性	○	○	○	×	×

[0041]

[Work example 5] Thermosetting polyimide resin 100 weight section of a bismaleimide triazine type, Organopolysiloxane 12 weight section, fused-quartz powder 185.7 weight section which were prepared by the reference example 3, KARUNA bow wax 2.9 weight section and benzoic acid aluminum 0.9 weight section were mixed uniformly, this was further cooled after kneading

with a 90 ° heating roller, and the hardenability resin composition of this invention was prepared. Subsequently, this was ground and transfermold shaping was carried out for 4 minutes under the conditions of 220 °, and 70 kg / cm<sup>2</sup>. Then, postcure of this hardening resin was carried out over 3 hours at 230 °. The various characteristics of the obtained hardening resin were shown in Table 3.

[0042]

[Comparative example 5] In Example 5, the hardenability resin composition was prepared like Example 5 except not using the organopolysiloxane prepared by the reference example 3. This was stiffened like Example 5. The various characteristics of this hardening resin were shown in Table 3.

[0043]

[Table 3]

測定項目	本発明	比較例
	実施例5	比較例5
スパイラルフロー (°)	53	44
曲げ弾性率 (kgf/mm <sup>2</sup> )	960	1220
接着性	○	×

[0044]

[Work example 6] Orthocresol-novolak-epoxy-resin (80 ° of softening temperature, weight per epoxy equivalent 220) 75 weight section, Fused silica 260 weight section, KARUNA bow wax 1 weight section, phenol novolak resin 35 weight section, Triphenylphosphine 0.6 weight section, organopolysiloxane 13 weight section prepared by the reference example 4, and 3-glycidoxypyriltrimetoxysilane 1.0 weight section were mixed uniformly, this was further cooled after kneading with a 90 ° heating roller, and the hardenability resin composition of this invention was prepared. Subsequently, this was ground and transfermold shaping was carried out for 3 minutes under the conditions of 150 °, and 70 kg / cm<sup>2</sup>. Then, postcure of this hardening resin was carried out over 4 hours at 180 °. The various characteristics of the obtained hardening resin were shown in Table 4.

[0045]

[Comparative example 6] In Example 6, the hardenability resin composition was prepared like Example 6 except not using the organopolysiloxane prepared by the reference example 4. This was stiffened like Example 6. The various characteristics of the obtained hardening resin were shown in Table 4.

[0046]

[Table 4]

測定項目	本発明	比較例
	実施例 6	比較例 6
スパイラルフロー (インチ)	7 5	5 5
成形収縮率 (%)	0. 3 5	0. 4 0
熱膨張率 ( $\times 10^{-6}/^{\circ}\text{C}$ )	2. 5 2	2. 7 1
曲げ弾性率 ( $\text{kgf}/\text{mm}^2$ )	1 1 2 0	1 4 2 0
吸水率 (%)	0. 4 5	0. 5 5
バリ (mm)	2	2
接着性	○	×
耐熱衝撃性	○	×
半田耐熱性	○	×

[0047]

[Work example 7] 3,4-epoxycyclohexyl 3,4-epoxy cyclohexane carboxylate 100 weight section, Organopolysiloxane 24 weight section prepared by 3 or 4-methylhexa HAIDOROFUTARIKKU anhydride 120.5 weight section, tin octylate 1.4 weight section, and the reference example 2 was mixed uniformly, and the hardenability resin composition of this invention was prepared. This was inserted into the nickel board of 1-mm thickness, was heated at 150 more \*\* after heating for 3 hours in 210 \*\* and 2 hours, and resin was stiffened. The adhesive strength to the nickel board of hardening resin was measured. This result was shown in Table 5.

[0048]

[Work example 8] In Example 7, the hardenability resin composition was prepared like Example 7 except having used the organopolysiloxane prepared by the reference example 4 instead of the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 7. The adhesive strength to the nickel board of the obtained hardening resin was measured. This result was shown in Table 5.

[0049]

[Comparative example 7] In Example 7, hardening resin was prepared like Example 7 except not using the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 7. The adhesive strength to the nickel board of the obtained hardening resin was measured. This result was shown in Table 5.

[0050]

[Table 5]

測定項目	本発明		比較例
	実施例 7	実施例 8	比較例 7
接着強度 (kgf/mm <sup>2</sup> )	6.5	6.2	5.0

[0051]

[Effect of the Invention] Since the hardenability resin composition of this invention has blended into a monad the organopolysiloxane which has an alkoxy silyl alkyl group and at least one with a carbon numbers of six or more alkyl group at a time as a (B) ingredient, Mobility is excellent before hardening and it has after hardening the feature that hardening resin excellent in flexibility and an adhesive property can be obtained.

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## TECHNICAL FIELD

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[Industrial Application]About a hardenability resin composition, in detail, this invention is excellent in mobility before hardening, and relates to the hardenability resin composition which serves as hardening resin excellent in flexibility and an adhesive property after hardening.

[0002]Since mechanical properties, such as electrical properties, such as the dielectric characteristics of the hardening resin produced by hardening this, volume resistivity, and electrical breakdown strength, or flexural strength, compressive strength, and impact strength, are excellent, the hardenability resin composition is used for the electrical and electric equipment and sealing resin for electronic devices, adhesives, resin for FRP, etc.

[0003]Generally, a hardenability resin composition has the upright hardening resin produced by hardening this, and Since [ lacking in flexibility and ] the rate of cure shrinkage at the time of hardening is large, If this is used as the electrical and electric equipment and sealing resin for electronic devices, in order to add big stress to the electrical and electric equipment and an electronic device, There was a problem of producing a crack in hardening resin itself, or destroying the electrical and electric equipment and an electronic device, or producing a crevice between the electrical and electric equipment and an electronic device, and hardening resin since the adhesive property over the electrical and electric equipment and electronic device of hardening resin is still lower. The coefficient of thermal expansion of the hardening resin produced by hardening this a hardenability resin composition to the coefficient of thermal expansion of the electrical and electric equipment and an electronic device Since it is large, If the resin seal electrical and electric equipment and an electronic device receive a thermo cycle, in order to add big stress to the electrical and electric equipment and an electronic device, There was a problem of producing a crack in hardening resin itself, or destroying the electrical and electric equipment and an electronic device, or producing a crevice between the electrical and electric equipment and an electronic device, and hardening resin since the adhesive property over the electrical and electric equipment and electronic device of hardening

resin is still lower. When water moreover invaded into the crevice between the crack or hardening resin produced by the cure shrinkage of a hardenability resin composition, or thermal expansion contraction, and the electrical and electric equipment and an electronic device, there was a problem of promoting degradation of the resin seal electrical and electric equipment and an electronic device.

[0004] Thus, in the hardenability resin composition, in order to low-stress-ize hardening resin, the flexibility of hardening resin is raised, and the hardenability resin composition of the versatility which makes the adhesive property over the electrical and electric equipment and electronic device of hardening resin come to improve is proposed. For example, an epoxy resin, a methylphenyl polysiloxane, the organopolysiloxane that consists of bifunctional siloxane units (D unit) which have an epoxy group, and trifunctional siloxane units (T unit), The hardenability resin composition which consists of an inorganic filler and a catalyst for hardening (refer to JP,56-145942,A), . Have an epoxy resin, an epoxy group or an amino group and a hydroxyl group, or at least one basis that can be hydrolyzed, respectively. The organopolysiloxane which consists of monofunctional siloxane units (M unit) or trifunctional siloxane units (T unit), and bifunctional siloxane units (D unit), The hardenability resin composition which consists of a hardening agent and an inorganic filler (refer to JP,56-136816,A), An epoxy resin, phenol resin, the hardenability resin composition that becomes a chain side chain from the dimethylpolysiloxane which has an epoxy group and a polyoxyalkylene group (refer to JP,60-58425,A), And the hardenability resin composition (refer to JP,64-51467,A) which consists of hardening resin and silicone rubber spherical pulverized coal is proposed.

[0005] However, the hardenability resin composition proposed by JP,56-145942,A and JP,56-136816,A, Since the organopolysiloxane which makes bifunctional siloxane units (D unit) indispensable is used, There was a fault that the glass transition point (Tg) of the obtained hardening resin fell, and it was remarkable especially when using Loh Sun for the organopolysiloxane which consists of  $2\text{SiO}_2/a_2$  unit (D unit) which has an epoxy group ( $\text{CH}_3$ ). The hardenability resin composition proposed by JP,60-58425,A, In order to use the dimethylpolysiloxane which has an epoxy group and a polyoxyalkylene group for a chain side chain, there was a fault that the obtained hardening resin had large absorptivity and it was not suitable as the electrical and electric equipment and sealing resin for electronic devices. The hardenability resin composition proposed by JP,64-51467,A, Although the flexibility of the hardening resin produced by hardening this was excellent, since the mobility of a hardenability resin composition was bad, there was a fault that the workability which carries out the resin seal of the electrical and electric equipment and the electronic device was bad, and this hardening resin had a still worse adhesive property over the electrical and electric equipment and an electronic device.

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## EFFECT OF THE INVENTION

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[Effect of the Invention]Since the hardenability resin composition of this invention has blended into a monad the organopolysiloxane which has an alkoxy silyl alkyl group and at least one with a carbon numbers of six or more alkyl group at a time as a (B) ingredient, Mobility is excellent before hardening and it has after hardening the feature that hardening resin excellent in flexibility and an adhesive property can be obtained.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention]This invention persons reached this invention, as a result of trying hard wholeheartedly, in order to solve the above-mentioned problem.

[0007]That is, the purpose of this invention is to provide the hardenability resin composition used as the hardening resin in which mobility was excellent in before hardening and flexibility and an adhesive property were excellent after hardening.

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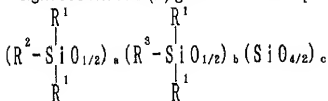
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## OPERATION

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[A means for solving a problem, and its operation] This invention is (A) hardening resin. 100 weight section and (B) general formula : [Formula 2]



{R<sup>1</sup> is a with a carbon number of five or less low-grade alkyl group or a phenyl group among a formula, R<sup>2</sup> is a basis chosen from the group which consists of a with a carbon number of five or less low-grade alkyl group, a phenyl group, and a hydrogen atom, and R<sup>3</sup> is a basis chosen from the group which consists of an epoxy group content organic group, an alkoxy silyl alkyl group, and a with a carbon numbers of six or more alkyl group. a is 0 or a positive number, b is a positive number, c is a positive number, a/c is the number of 0-4, and b/c is the number of 0.05-4, and (a+b)/c is the number of 0.2-4. It is expressed with} and related with the hardenability resin composition which consists of 0.1 to organopolysiloxane 500 weight section which has an alkoxy silyl alkyl group and at least one with a carbon numbers of six or more alkyl group at a time in a monad.

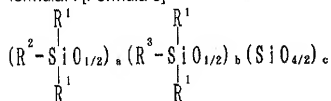
[0009]The hardenability resin composition of this invention is explained in detail.

[0010](A) Hardening resin is a substrate of this invention. (A) Conventionally, especially if an ingredient is publicly known hardening resin, it will not be limited. (A) As an ingredient specifically, Phenol resin, formaldehyde resins, xylene resin, xylene-formaldehyde resin, ketone formaldehyde resins, furan resin, urea resin, imide resin, melamine resin, an alkyd resin, unsaturated polyester resin, aniline resin, sulfone amide resin, Silicone resin, epoxy resins, and these copolymer resin are illustrated, and hardening resin of the above-mentioned illustration can also be used combining two or more sorts. In hardening resin of these

illustration, it is hardening resin especially chosen from a group which consists of an epoxy resin, phenol resin, imide resin, and silicone resin preferably as a (A) ingredient. Hardening resin hardened with high energy beams which a curing means in particular of the (A) ingredient is not limited, for example, are hardened with heat, such as hardening resin, ultraviolet rays, or radiation, and hardening resin hardened with humidity are mentioned. The (A) ingredient is liquefied at a room temperature, or it may be hardening resin of which state of a solid state, and it may contain an organic solvent etc.

[0011](A) A hardening agent, a hardening accelerator, a bulking agent, a photosensitizer, higher-fatty-acid metal salt, an ester system wax, a plasticizer, etc. can be blended with an ingredient as ingredients other than hardening resin of the above-mentioned illustration. (A) As a hardening agent which can be blended with an ingredient specifically, Organic acid, such as carboxylic acid and sulfonic acid, and an anhydride of those, an organic hydroxy compound, a silanol group, An amino compound of an organic silicon compound and the first class which have bases, such as an alkoxy group or a halogeno group, or the second class can be illustrated, and it can also be used, combining these two or more sorts. As a hardening accelerator which can be blended with the (A) ingredient, specifically, Organophosphorus compounds, such as organic metallic compounds, such as the third class amine compound, aluminum, and a zirconium, and phosphine, a different ring type amine compound, a boron complex compound, organic ammonium salt, organic sulfonium salt, organic peroxide, etc. are illustrated. As a bulking agent which can be blended with the (A) ingredient, specifically, Glass fiber, asbestos, an alumina fiber, alumina, and silica. Fibrous fillers, such as ceramic fiber used as an ingredient, a boron fiber, a zirconia fiber, silicon carbide fiber, a metal fiber, polyester fiber, an aramid fiber, a nylon fiber, a phenol fiber, and natural animals-and-plants textiles, fused silica, precipitation silica, fumed silica, pyrogenic silica, a zinc oxide, Calcination clay, carbon black, a glass bead, alumina, talc, calcium carbonate, clay, aluminium hydroxide, barium sulfate, a titanium dioxide, aluminium nitride, silicon carbide, magnesium oxide, beryllium oxide, kaolin, mica, Particulate matter-like bulking agents and these mixtures, such as zirconia, are illustrated.

[0012](B) Organopolysiloxane is an ingredient for raising the mobility of a hardenability resin composition of this invention, raising the flexibility of hardening resin produced by hardening this, and raising an adhesive property over adherends, such as metal, and is a general formula. : [Formula 3]



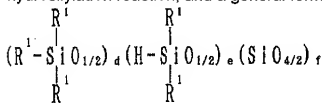
It is organopolysiloxane come out of and expressed.  $R^1$  is a with a carbon number of five or less low-grade alkyl group or a phenyl group among an upper type, and, specifically, a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group are illustrated as a with a carbon number of five or less low-grade alkyl group. Among an upper type,  $R^2$  is a basis chosen from the group which consists of a with a carbon number of five or less low-grade alkyl group, a phenyl group, and a hydrogen atom, and, specifically, a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group are illustrated as a with a carbon number of five or less of  $R^2$  low-grade alkyl group.  $R^3$  is a basis chosen from the group which consists of an epoxy group content organic group, an alkoxy silyl alkyl group, and a with a carbon numbers of six or more alkyl group among an upper type, As an epoxy group content organic group of  $R^3$ , specifically, 2-glycidoxy ethyl group, 3-glycidoxy propyl group, 4-glycidoxybutyl group, 5-glycidoxy pentyl group, 2-(3,4-epoxycyclohexyl) ethyl group, 3-(3,4-epoxycyclohexyl) propyl group, 4-(3,4-epoxycyclohexyl) A butyl group is illustrated and as an alkoxy silyl alkyl group of  $R^3$  specifically, A trimethoxysilyl ethyl group, a trimethoxysilylpropyl group, a trimethoxysilyl butyl group, a trimethoxysilyl pentyl group, a triethoxy silyl ethyl group, a triethoxy silyl propyl group, a triethoxy silyl butyl group, a methyl dimethoxy silyl ethyl group, A methyl dimethoxy silyl propyl group, a dimethyl methoxy silylethyl group, and a dimethyl methoxy silylpropyl group are illustrated, and as a with a carbon numbers of six or more of  $R^3$  alkyl group specifically, A hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, the dodecyl, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, and an octadecyl group are illustrated, n-hexyl group, n-heptyl group, n-octyl group, n-nonyl group, n-decyl group, n-undecyl group, n-dodecyl, n-tridecyl group, n-tetradecyl group, an n-pentadecyl group, n-hexadecyl group, n-heptadecyl group, and n-octadecyl group are preferred. (B) It is required for the carbon number of the alkyl group of  $R^3$  to be six or more in an ingredient, Although the maximum in particular was not limited, when this is blended with the (A) ingredient, (A) As for the carbon number of the alkyl group of  $R^3$ , since the compatibility of an ingredient and the (B) ingredient is good and the flexibility and adhesive property of resin after hardening the hardening resin constituent obtained are good, it is preferred that it is the range of 6-30.

[0013]a is 0 or a positive number which shows the number of monofunctional siloxane units (M unit) which do not have an epoxy group content organic group, an alkoxy silyl alkyl group, or a with a carbon numbers of six or more alkyl group among an upper type, b is a positive number which shows the number of monofunctional siloxane units (M unit) which have an epoxy group content organic group, an alkoxy silyl alkyl group, or a with a carbon numbers of six or more alkyl group, c is a positive number which shows the number of tetrafunctional siloxane units (Q

unit), each ratio and  $a/c$  are the number of the ranges of 0-4, and  $b/c$  is the number of the ranges of 0.05-4, and  $(a+b)/c$  is the number of the ranges of 0.2-4. This is for the compatibility of the (A) ingredient and the (B) ingredient to fall that monofunctional siloxane units (M unit) cannot surpass four pieces, but monofunctional siloxane units (M unit) are less than 0.2 piece to one tetrafunctional siloxane units (Q unit). In a hardenability resin composition of this invention, in order for the compatibility of the (A) ingredient and the (B) ingredient to be excellent, (B) It is because monofunctional siloxane units (M unit) which have an epoxy group content organic group in an ingredient, an alkoxy silyl alkyl group, or a with a carbon numbers of six or more alkyl group need to be at least 0.05 piece to one tetrafunctional siloxane units (Q unit). (B) Although an ingredient is liquefied at a room temperature, or it is a solid state and the molecular weight in particular is not limited, since compatibility with the (A) ingredient is good, it is preferred that it is the range of 500-500,000.

[0014] In a hardenability resin composition of this invention, the (B) ingredient, Since it has an alkoxy silyl alkyl group and a with a carbon numbers of six or more alkyl group, (A) Since the flexibility of hardening resin obtained by being incorporated into a resin matrix of an ingredient improves and the (B) ingredient consists of a  $\text{SiO}_2$  unit (Q unit), it has the advantage of excelling in flexibility and an adhesive property.

[0015] The above-mentioned (B) ingredients are the bottom of existence of a catalyst for a hydrosilylation reaction, and a general formula, for example. : [Formula 4]



$\{\text{R}^1$  is a with a carbon number of five or less low-grade alkyl group or a phenyl group among a formula.  $d$  is 0 or a positive number,  $e$  is a positive number,  $f$  is a positive number,  $d/f$  is the number of 0-4, and  $e/f$  is the number of 0.05-4, and  $(d+e)/f$  is the number of 0.2-4. It can prepare by making the organopolysiloxane expressed with} carry out the addition reaction of the organic compound which has an epoxy group and aliphatic unsaturated bonds if needed to an alkoxy silylalkene and a with a carbon numbers of six or more alkene.

[0016] In a hardenability resin composition of this invention, loadings of the (B) ingredient are 0.1 - 500 weight section to (A) ingredient 100 weight section.

It is 0.5 to 100 weight section preferably.

This is for the flexibility of hardening resin obtained as loadings of the (B) ingredient are less than 0.1 weight sections to (A) ingredient 100 weight section not to improve.

When this surpasses 500 weight sections, it is for a mechanical strength of obtained hardening

resin to fall remarkably.

[0017]A hardenability resin composition of this invention can be prepared by mixing the (A) ingredient and the (B) ingredient uniformly. (A) A method in particular of mixing an ingredient and the (B) ingredient is not limited, but specifically, (A) After blending and carrying out the premix of the (B) ingredient at the time of a method of blending the (B) ingredient with an ingredient directly, and (A) ingredient preparation, a method of blending additive agents, such as a bulking agent, with the (A) ingredient and a method of blending with the (B) ingredient various kinds of additive agents blended with the (A) ingredient one by one are illustrated. (A) Although there is no limitation and a mixed device is chosen by gestalt of versatility [ingredient / the (A) ingredient or / (B) ], such as a liquid, a solid state, and powder, especially as a mixed device which mixes an ingredient and the (B) ingredient, Specifically, a continuous mixer of one axis or two axes, 2 rolls, a loss mixer, and a kneader mixer are illustrated.

[0018]Since mobility is excellent before hardening, a hardenability resin composition of this invention can be used by methods, such as a transfer mold, injection molding, potting, casting, powder coating, dip coating, and dropping. Since after hardening becomes hardening resin excellent in flexibility and an adhesive property, a hardenability resin composition of this invention can be used for a hardenability resin composition for closing electrical and electric equipment and an electronic device, adhesives, etc.

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[Translation done.]

\* NOTICES \*

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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EXAMPLE

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[Example]An example explains the hardenability resin composition of this invention in detail. Among the example, the value of viscosity is a value measured in 25 \*\*, and measured the various characteristics of a hardenability resin composition and hardening resin by the following method.

[0020]O Spiral flow : it measured by the method according to an EMMI standard.

O Molding shrinkage : It measured by the method according to JIS-K-6911.

O Coefficient of thermal expansion : The hardening resin fabricated to 5mmx5mmx16mm was measured using the thermal expansion meter (DL-7000 by a vacuum science-and-engineering company). The value of a coefficient of thermal expansion is a value from a room temperature to a glass transition point.

O Glass transition point (Tg) : it measured by coefficient-of-thermal-expansion measurement.

O Rate of bending flexibility : It measured by the method according to JIS-K-6911.

O Water absorption : After making into the temperature of 121 \*\*, and 100% of humidity the hardening resin fabricated to 2 inch x0.5 inch x0.25 inch and humidifying it for 20 hours, it asked by measuring the weight increment of the hardening resin.

O Barricade : The 20-micrometer-deep slot was used and barricade length was measured.

O Adhesive property : After inserting the hardenability resin composition into 42 alloy board and the copper plate and stiffening this, the adhesive property at the time of removing hardening resin was judged by O (good) and x (poor).

O Thermal shock resistance : 20 resin seal semiconductor devices (chip size 36 mm<sup>2</sup>, and package 2.0 mm in thickness) are fabricated, This was performed at -196 \*\*<-->+150 \*\*, the heat cycle test was done in the cycle for 1 minute, the sealing resin surface was observed with the stereoscopic microscope after 150 cycles, and the case where they were \*\* and 11 pieces or more about the case where they are O and 6-10 pieces about the case where the number of the mold goods in which the crack went into the surface is five or less pieces was made into x.

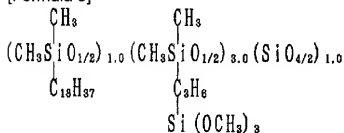
O Solder heat resistance : 20 resin seal semiconductor devices (chip size  $36 \text{ mm}^2$ , and package 2.0 mm in thickness) were fabricated, this was promptly immersed in a 240 \*\* solder bath after 72-hour neglect under 85%RH conditions at 85 \*\* for 1 hour, and the sealing resin surface was observed with the stereoscopic microscope. The case where they were \*\* and 11 pieces or more about the case where they are O and 6-10 pieces about the case where the number of the mold goods in which the crack went into the surface is five or less pieces was made into x.

[0021]

[Reference example 1] making allyl trimethoxysilane and 1-OKUTADEN tetrakis (dimethyl siloxy) Silang react to agitating equipment, a flowing-back condenser tube, and a 4 mouth flask with a thermometer under existence of chloroplatinic acid in toluene -- a yellowish brown color -- transparent organopolysiloxane was prepared. The viscosity of this organopolysiloxane was 24 centipoises and the refractive index was 1.4358. When  $^1\text{H}$ -nuclear-magnetic-resonance-spectrum analysis (following, NMR),  $^{13}\text{C}$ -NMR, and  $^{29}\text{Si}$ -NMR analyzed this organopolysiloxane, what is expressed with the following structural formula was checked.

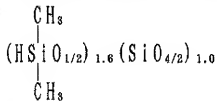
[0022]

[Formula 5]



[0023]

[Reference example 2] It is a formula to agitating equipment, a flowing-back condenser tube, and a 4 mouth flask with a thermometer. : [Formula 6]



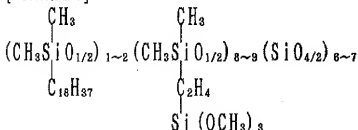
Came out, reacted the organopolysiloxane (0.92 % of the weight of content of 46 centipoise viscosity and a silicon atom absorbed water matter atom) expressed in toluene, vinyltrimethoxysilane was made to react to 1-octadecene under existence of a chloroplatinic acid catalyst, and water-white organopolysiloxane was prepared. The viscosity of this organopolysiloxane was 97 centipoises and the refractive index was 1.4386. When  $^1\text{H}$ -NMR,



$^{13}\text{C}$ -NMR, and  $^{29}\text{Si}$ -NMR analyzed this organopolysiloxane, what is expressed with the following structural formula was checked.

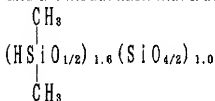
[0024]

[Formula 7]



[0025]

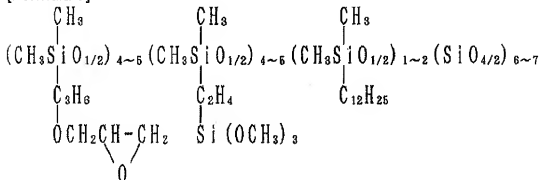
[Reference example 3] It is a formula to agitating equipment, a flowing-back condenser tube, and a 4 mouth flask with a thermometer. : [Formula 8]



Come out and the organopolysiloxane (0.92 % of the weight of content of 46 centipoise viscosity and a silicon atom absorbed water matter atom) expressed in toluene, Allyl glycidyl ether was made to react to 1-dodecen and vinyltrimetoxysilane under existence of a chloroplatinic acid catalyst, and transparent brown organopolysiloxane was prepared. The viscosity of this organopolysiloxane was 142 centipoises and the refractive index was 1.4475. When  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and  $^{29}\text{Si}$ -NMR analyzed this organopolysiloxane, what is expressed with the following structural formula was checked.

[0026]

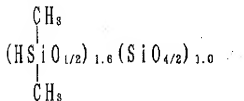
[Formula 9]



[0027]

[Reference example 4] It is a formula to agitating equipment, a flowing-back condenser tube,

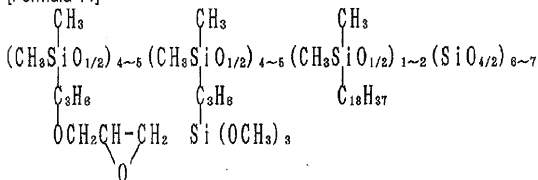
and a 4 mouth flask with a thermometer. : [Formula 10]



Came out, reacted the organopolysiloxane (0.92 % of the weight of content of 46 centipoise viscosity and a silicon atom absorbed water matter atom) expressed in toluene, vinyltrimetoxysilane was made to react to 1-octadecene under existence of chloroplatinic acid, and water-white organopolysiloxane was prepared. The viscosity of \*\*\*\* organopolysiloxane was 97 centipoises and the refractive index was 1.4386. when  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and  $^{29}\text{Si}$ -NMR analyzed this organopolysiloxane, the following structural formula and the thing come out and expressed were checked.

[0028]

[Formula 11]



[0029]

[Work example 1] Phenol novolak resin (80 \*\* of softening temperature, hydroxyl equivalent 100) 100 weight section, Organopolysiloxane 8.9 weight section, fused-quartz powder 185.7 weight section which were prepared by the reference example 1, Hexamethylenetetramine 11.4 weight section, 3-glycidioxypropyltrimetoxysilane 1.0 weight section, and KARUNA bow wax 2.9 weight section were mixed uniformly, this was further cooled after kneading with a 90 \*\* heating roller, and the hardenability resin composition of this invention was prepared. Subsequently, this was ground and transfer moulding was carried out for 3 minutes under the conditions of 175 \*\*, and 70 kg / cm<sup>2</sup>. Then, postcure of the hardening resin was carried out over 2 hours at 150 \*\*. The various characteristics of the obtained hardening resin were shown in Table 1.

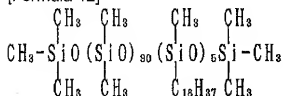
[0030]

[Comparative example 1] In Example 1, the hardenability resin composition was prepared like Example 1 except having used the organopolysiloxane expressed with a lower type instead of

the organopolysiloxane prepared by the reference example 1. This was stiffened like Example 1. The various characteristics of the obtained hardening resin were shown in Table 1.

[0031]

[Formula 12]



[0032]

[Comparative example 2] In Example 1, the hardenability resin composition was prepared like Example 1 except not using the organopolysiloxane prepared by the reference example 1. This was stiffened like Example 1. The various characteristics of the obtained hardening resin were shown in Table 1.

[0033]

[Table 1]

測定項目	本発明	比較例	
	実施例 1	比較例 1	比較例 2
スパイラルフロー (1/f)	3.9	3.4	3.1
成形収縮率 (%)	0.23	0.20	0.31
熱膨張率 ( $\times 10^{-6}/^{\circ}\text{C}$ )	1.19	1.05	1.50
ガラス転移点 ( $^{\circ}\text{C}$ )	161	138	156
曲げ弾性率 ( $\text{kgf}/\text{mm}^2$ )	1200	1260	1350
吸水率 (%)	0.39	0.56	0.51

[0034]

[Work example 2]  $\text{CH}_3\text{SiO}_{3/40}$  mol of 2 unit %, and  $\text{C}_6\text{H}_5(\text{CH}_3)\text{SiO}_{2/10}$  mol of 2 unit %, It consists of  $\text{C}_6\text{H}_5\text{SiO}_{3/40}$  mol of 2 unit %, and  $(\text{C}_6\text{H}_5)_2\text{SiO}_{2/10}$  mol of 2 unit %, Silicone resin 50 weight section and cresol novolak epoxy resin (80 \*\* of softening temperatures) which contain a silicon atom absorbed water acid radical 5% of the weight Silicone epoxy resin 100 weight section which consists of weight per epoxy equivalent 220 50 weight section, Organopolysiloxane 8.0 weight section, fused-quartz powder 284.6 weight section which were prepared by the reference example 2, Aluminum acetylacetonate 3.5 weight section, 3-glycidoxypopyltrimetoxysilane 1.0 weight section, and KARUNA bow wax 3.8 weight section were mixed uniformly, this was further cooled after kneading with a 90 \*\* heating roller, and the

hardenability resin composition of this invention was prepared. Subsequently, this was ground and transfermold shaping was carried out for 2 minutes under the conditions of 175 \*\*, and 70 kg / cm<sup>2</sup>. Then, postcure of this hardening resin was carried out over 12 hours at 180 \*\*. The various characteristics of the obtained hardening resin were shown in Table 2.

[0035]

[Work example 3] In Example 2, the hardenability resin composition was prepared like Example 2 except having used the organopolysiloxane prepared by the reference example 3 instead of the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 2. The various characteristics of the obtained hardening resin were shown in Table 2.

[0036]

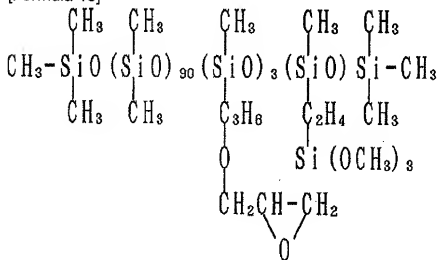
[Work example 4] In Example 2, the hardenability resin composition was prepared like Example 2 except having used the organopolysiloxane prepared by the reference example 4 instead of the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 2. The various characteristics of the obtained hardening resin were shown in Table 2.

[0037]

[Comparative example 3] In Example 2, the hardenability resin composition was prepared like Example 2 except having used the organopolysiloxane expressed with the following structural formula instead of the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 2. The various characteristics of the obtained hardening resin were shown in Table 2.

[0038]

[Formula 13]



[0039]

[Comparative example 4] In Example 2, the hardenability resin composition was prepared like Example 2 except not adding the organopolysiloxane prepared by the reference example 2.

This was stiffened like Example 2. The various characteristics of the obtained hardening resin were shown in Table 2.

[0040]

[Table 2]

測定項目	本 発 明			比 較 例	
	実施例2	実施例3	実施例4	比較例3	比較例4
スパイラルフロー (inch)	45	44	42	40	35
熱膨張率 ( $\times 10^{-6}/^{\circ}\text{C}$ )	2.26	2.18	2.15	2.90	2.75
曲げ弾性率 ( $\text{kgf}/\text{mm}^2$ )	1110	1090	1150	1250	1520
吸水率 (%)	0.40	0.39	0.38	0.56	0.47
バリ (mm)	3	5	4	15	4
接着性	○	○	○	△	×
耐熱衝撃性	○	○	○	△	×
半田耐熱性	○	○	○	×	×

[0041]

[Work example 5] Thermosetting polyimide resin 100 weight section of a bismaleimide triazine type, Organopolysiloxane 12 weight section, fused-quartz powder 185.7 weight section which were prepared by the reference example 3, KARUNA bow wax 2.9 weight section and benzoic acid aluminum 0.9 weight section were mixed uniformly, this was further cooled after kneading with a 90 ° heating roller, and the hardenability resin composition of this invention was prepared. Subsequently, this was ground and transfermold shaping was carried out for 4 minutes under the conditions of 220 °, and 70 kg / cm<sup>2</sup>. Then, postcure of this hardening resin was carried out over 3 hours at 230 °. The various characteristics of the obtained hardening resin were shown in Table 3.

[0042]

[Comparative example 5] In Example 5, the hardenability resin composition was prepared like Example 5 except not using the organopolysiloxane prepared by the reference example 3. This was stiffened like Example 5. The various characteristics of this hardening resin were shown in Table 3.

[0043]

[Table 3]

測定項目	本発明	比較例
	実施例5	比較例5
スパイラルフロー (inch)	53	44
曲げ弾性率 (kgf/mm <sup>2</sup> )	960	1220
接着性	○	×

[0044]

[Work example 6] Orthocresol-novolac-epoxy-resin (80 \*\* of softening temperature, weight per epoxy equivalent 220) 75 weight section, Fused silica 260 weight section, KARUNA bow wax 1 weight section, phenol novolak resin 35 weight section, Triphenylphosphine 0.6 weight section, organopolysiloxane 13 weight section prepared by the reference example 4, and 3-glycidoxypolytrimetoxysilane 1.0 weight section were mixed uniformly, this was further cooled after kneading with a 90 \*\* heating roller, and the hardenability resin composition of this invention was prepared. Subsequently, this was ground and transfermold shaping was carried out for 3 minutes under the conditions of 150 \*\*, and 70 kg / cm<sup>2</sup>. Then, postcure of this hardening resin was carried out over 4 hours at 180 \*\*. The various characteristics of the obtained hardening resin were shown in Table 4.

[0045]

[Comparative example 6] In Example 6, the hardenability resin composition was prepared like Example 6 except not using the organopolysiloxane prepared by the reference example 4. This was stiffened like Example 6. The various characteristics of the obtained hardening resin were shown in Table 4.

[0046]

[Table 4]

測定項目	本発明	比較例
	実施例6	比較例6
スパイラルフロー (inch)	75	55
成形収縮率 (%)	0.35	0.40
熱膨張率 ( $\times 10^{-6}/^{\circ}\text{C}$ )	2.52	2.71
曲げ弾性率 ( $\text{kgf}/\text{mm}^2$ )	1120	1420
吸水率 (%)	0.45	0.55
バリ (mm)	2	2
接着性	○	×
耐熱衝撃性	○	×
半田耐熱性	○	×

[0047]

[Work example 7] 3,4-epoxycyclohexyl 3,4-epoxy cyclohexane carboxylate 100 weight section, Organopolysiloxane 24 weight section prepared by 3 or 4-methylhexa HAIDOROFUTARIKKU anhydride 120.5 weight section, tin octylate 1.4 weight section, and the reference example 2 was mixed uniformly, and the hardenability resin composition of this invention was prepared. This was inserted into the nickel board of 1-mm thickness, was heated at 150 more \*\* after heating for 3 hours in 210 \*\* and 2 hours, and resin was stiffened. The adhesive strength to the nickel board of hardening resin was measured. This result was shown in Table 5.

[0048]

[Work example 8] In Example 7, the hardenability resin composition was prepared like Example 7 except having used the organopolysiloxane prepared by the reference example 4 instead of the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 7. The adhesive strength to the nickel board of the obtained hardening resin was measured. This result was shown in Table 5.

[0049]

[Comparative example 7] In Example 7, hardening resin was prepared like Example 7 except not using the organopolysiloxane prepared by the reference example 2. This was stiffened like Example 7. The adhesive strength to the nickel board of the obtained hardening resin was measured. This result was shown in Table 5.

[0050]

[Table 5]

測 定 項 目	本 発 明		比較例
	実施例 7	実施例 8	比較例 7
接着強度 (kgf/mm <sup>2</sup> )	6.5	6.2	5.0

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[Translation done.]



## CURABLE RESIN COMPOSITION

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JP3466239 (B2)

Inventor(s): MORITA YOSHII; SASAKI ATSUSHI; TACHIBANA TAKASHI

Applicant(s): DOW CORNING TORAY SILICONE

Classification:

- International: C08G59/30; C08G59/40; C08L61/04; C08L61/06; C08L63/00; C08L79/06; C08L83/04; C08L83/06; C08L101/00; C08G59/00; C08L61/00; C08L63/00; C08L79/00; C08L83/00; C08L101/00; (IPC1-7): C08L83/06; C08G59/30; C08G59/40; C08L61/06; C08L63/00; C08L79/06; C08L101/00

- European:

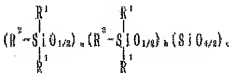
Application number: JP19930225165 19930818

Priority number(s): JP19930225165 19930818

## Abstract of JP 7053870 (A)

**PURPOSE:** To obtain the composition, excellent in fluidity before curing and flexibility and adhesion after the curing and useful as a sealing resin for electrical and electronic elements by blending a curable resin with a specific organopolysiloxane.

**CONSTITUTION:** This curable resin composition comprises (A) 100 pts.wt. curable resin and (B) 0.1-500 pts.wt. organopolysiloxane, expressed by the formula ( $R<1>$ ) is a <=6C alkyl or phenyl;  $R<2>$  is a <=6C alkyl, phenyl or H;  $R<3>$  is an epoxy group-containing organic group, an alkoxyalkyl or a >=6C alkyl; (a) is 0 or a positive number; (b) and (c) are positive numbers; (a/c) is 0-4; (b/c) is 0.05-4; [(a+b)/c] is 0.2-4; and having at least one each of the alkoxyalkyl group and >=6C alkyl group in one molecule. Furthermore, the component (A) is preferably selected from the group consisting of an epoxy resin, a phenolic resin, an imide resin and a silicone resin and the component (B) has preferably further an epoxy group-containing organic group.



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特開平7-53870

(43) 公開日 平成7年(1995)2月28日

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C 0 8 L 61/06	I N B			
63/00	N K B			

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(21) 出願番号	特願平5-225165	(71) 出願人	000110077 東レ・ダウコーニング・シリコン株式会社 東京都中央区日本橋室町2丁目3番16号
(22) 出願日	平成5年(1993)8月18日	(72) 発明者	森田 好次 千葉県市原市千種海岸2番2 東レ・ダウコーニング・シリコン株式会社研究開発本部内
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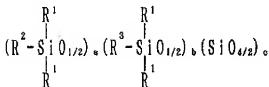
## (54) 【発明の名称】 硬化性樹脂組成物

## (57) 【要約】

【目的】 硬化前には流動性が優れ、硬化後には可撓性および接着性が優れた硬化樹脂となる硬化性樹脂組成物を提供する。

【構成】 (A) 硬化性樹脂 100重量部および(B)一般式:

【化1】



【式中、R<sup>1</sup>は炭素数6以下の低級アルキル基またはフェニル基であり、R<sup>2</sup>は炭素数6以下の低級アルキル基、フェニル基および水素原子からなる群から選択される基であり、R<sup>3</sup>はエポキシ基含有有機基、アルコキシシリルアルキル基および炭素数6以上のアルキル基からなる群から選択される基である。また、aは0または正数であり、bは正数であり、cは正数であり、a/cは

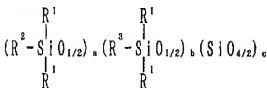
0~4の数であり、b/cは0.05~4の数であり、かつ(a+b)/cは0.2~4の数である。}で表され、一分子中にアルコキシシリルアルキル基と炭素数6以上のアルキル基とを少なくとも1個づつ有するオルガノポリシロキサン 0.1~500重量部からなる硬化性樹脂組成物。

【特許請求の範囲】

【請求項1】 (A) 硬化性樹脂

00重量部および(B)一般式:

【化1】



【式中、R<sup>1</sup>は炭素数5以下の低級アルキル基またはフェニル基であり、R<sup>2</sup>は炭素数6以下の低級アルキル基、フェニル基および水素原子からなる群から選択される基であり、R<sup>3</sup>はエポキシ基含有有機基、アルコキシシリルアルキル基および炭素数6以上のアルキル基からなる群から選択される基である。また、aは0または正数であり、bは正数であり、cは正数であり、a/cは0~4の数であり、b/cは0.05~4の数であり、かつ(a+b)/cは0.2~4の数である。】で表され、一分子中にアルコキシシリルアルキル基と炭素数6以上のアルキル基とを少なくとも1個づつ有するオルガノポリシロキサン0.1~600重量部からなる硬化性樹脂組成物。

【請求項2】 (A)成分がエポキシ樹脂、フェノール樹脂、イミド樹脂およびシリコン樹脂からなる群から選択される硬化性樹脂であることを特徴とする請求項1記載の硬化性樹脂組成物。

【請求項3】 (B)成分が一分子中にエポキシ基含有有機基とアルコキシシリルアルキル基と炭素数6以上のアルキル基とを少なくとも1個づつ有するオルガノポリシロキサンであることを特徴とする請求項1記載の硬化性樹脂組成物。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は硬化性樹脂組成物に関し、詳しくは、硬化前には流動性が優れ、硬化後には可塑性および接着性が優れた硬化樹脂となる硬化性樹脂組成物に関する。

【0002】 硬化性樹脂組成物は、これを硬化して得られた硬化樹脂の誘電特性、体積低抗率および絶縁破壊強度等の電気的特性あるいは曲げ強度、圧縮強度および衝撃強度等の機械的特性が優れているため、電気・電子素子用封止樹脂、接着剤、FRP用樹脂等々に使用されている。

【0003】 硬化性樹脂組成物は、これを硬化して得られた硬化樹脂が、一般に剛直で可塑性に乏しく、また硬化時の硬化収縮率が大きいため、これを電気・電子素子用封止樹脂として使用すると、電気・電子素子に対して大きな応力加わると、硬化樹脂自体に亀裂が生じたり、あるいは電気・電子素子を破壊したり、さらに硬化

樹脂の電気・電子素子に対する接着性が低いため、電気・電子素子と硬化樹脂との間に隙間を生じたりするという問題があった。また、硬化性樹脂組成物は、これを硬化して得られた硬化樹脂の熱膨張係数が電気・電子素子の熱膨張係数に対して大きいため、樹脂封止電気・電子素子がヒートサイクルを受けると、電気・電子素子に対して大きな応力加わると、硬化樹脂自体に亀裂が生じたり、あるいは電気・電子素子を破壊したり、さらに硬化樹脂の電気・電子素子に対する接着性が低いため、

10 電気・電子素子と硬化樹脂との間に隙間を生じたりするという問題があった。そのうえ、硬化性樹脂組成物の硬化収縮あるいは熱膨張収縮によって生じた亀裂または硬化樹脂と電気・電子素子との隙間に水が侵入することにより、樹脂封止電気・電子素子の劣化を促進するという問題があった。

【0004】 このよう、硬化性樹脂組成物において、硬化樹脂を低応力化するために硬化樹脂の可能性を向上させたり、また硬化樹脂の電気・電子素子に対する接着性を向上させてなる種々の硬化性樹脂組成物が提案されている。例えば、エポキシ樹脂、メチルフェニルポリシロキサン、エポキシ基を有する二官能性シロキサン単位(D単位)と三官能性シロキサン単位(T単位)からなるオルガノポリシロキサン、無機質充填剤および硬化用触媒からなる硬化性樹脂組成物(特開昭56-145942号公報参照)、エポキシ樹脂、エポキシ基またはアミノ基および水酸基または加水分解可能な基をそれぞれ少なくとも1個有する、一官能性シロキサン単位(M単位)または三官能性シロキサン単位(T単位)と二官能性シロキサン単位(D単位)からなるオルガノポリシロキサン、硬化剤および無機質充填剤からなる硬化性樹脂組成物(特開昭56-136816号公報参照)、エポキシ樹脂、フェノール樹脂、分子鎖鎖鎖にエポキシ基とポリオキシアルキレン基を有するジメチルポリシロキサンからなる硬化性樹脂組成物(特開昭60-58425号公報参照)、および硬化性樹脂とシリコンゴム球状微粉体からなる硬化性樹脂組成物(特開昭64-51467号公報参照)が提案されている。

【0005】 しかし、特開昭56-145942号公報および特開昭56-136816号公報により提案された硬化性樹脂組成物は、二官能性シロキサン単位(D単位)を必須とするオルガノポリシロキサンを使用しているので、得られた硬化樹脂のガラス転移点(Tg)が低下するという欠点があり、特に、エポキシ基を有する(CH<sub>3</sub>)<sub>2</sub>SiO<sub>2</sub>単位(D単位)からなるオルガノポリシロキサンをロキサンを使用する場合は顕著であった。特開昭60-58425号公報により提案された硬化性樹脂組成物は、分子鎖鎖鎖にエポキシ基とポリオキシアルキレン基を有するジメチルポリシロキサンを使用するため、得られた硬化樹脂は吸水性が大きく、電気・電子素子用封止樹脂としては適さないという欠点があっ

た。さらに、特開昭64-51467号公報により提案された硬化性樹脂組成物は、これを硬化して得られた硬化樹脂の可撓性が優れるものの、硬化性樹脂組成物の流動性が悪いため、電気・電子素子を樹脂封止する作業性が悪く、さらにこの硬化樹脂は電気・電子素子に対する接着性が悪いという欠点があった。

【0006】

【発明が解決しようとする問題点】 本発明者らは、上記問題点を解決するため鋭意努力した結果、本発明に到達した。

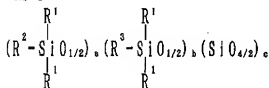
【0007】 すなわち、本発明の目的は、硬化前には流動性が優れ、硬化後には可撓性および接着性が優れた硬化樹脂となる硬化性樹脂組成物を提供することにある。

【0008】

【問題点を解決するための手段およびその作用】 本発明は、(A)硬化性樹脂 100

重量部および(B)一般式：

【化2】



【式中、R<sup>1</sup>は炭素数5以下の低級アルキル基またはフェニル基であり、R<sup>2</sup>は炭素数5以下の低級アルキル基、フェニル基および水素原子からなる群から選択される基であり、R<sup>3</sup>はエポキシ基含有有機基、アルコキシシリルアルキル基および炭素数6以上のアルキル基からなる群から選択される基である。また、aは0または正数であり、bは正数であり、cは正数であり、a/cは0~4の数であり、b/cは0.05~4の数であり、かつ(a+b)/cは0.2~4の数である。】で表され、一分子中にアルコキシシリルアルキル基と炭素数6以上のアルキル基とを少なくとも1個づつ有するオルガノポリシロキサン。1~500重量部からなる硬化性樹脂組成物に関する。

【0009】 本発明の硬化性樹脂組成物について詳細に説明する。

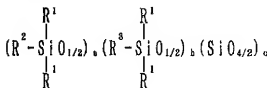
【0010】 (A)硬化性樹脂は、本発明の基材である。(A)成分は従来公知の硬化性樹脂であれば特に限定されない。(A)成分として、具体的には、フェノール樹脂、ホルムアルデヒド樹脂、キシレン樹脂、キシレンホルムアルデヒド樹脂、ケトンホルムアルデヒド樹脂、フラン樹脂、尿素樹脂、イミド樹脂、メラミン樹脂、アルキッド樹脂、不飽和ポリエステル樹脂、アクリン樹脂、スルホンアミド樹脂、シリコン樹脂、エポキシ樹脂およびこれらの共重合体樹脂が例示され、上記例示の硬化性樹脂を2種以上を組み合わせ使用することもできる。これら例示の硬化性樹脂において、特に、(A)成分

として好ましくは、エポキシ樹脂、フェノール樹脂、イミド樹脂およびシリコン樹脂からなる群から選択される硬化性樹脂である。なお、(A)成分の硬化手段は特に限定されず、例えば、熱により硬化する硬化性樹脂、紫外線または放射線等の高エネルギー線により硬化する硬化性樹脂、湿気により硬化する硬化性樹脂が挙げられる。また、(A)成分は室温で液状または固體状のいずれの状態の硬化性樹脂であってもよく、有機溶剤等を含んでいるもよい。

【0011】 (A)成分には、上記例示の硬化性樹脂以外の成分として、硬化剤、硬化促進剤、充填剤、光増感剤、高級脂肪酸金属塩、エステル系ワックス、可塑剤等を配合することができる。(A)成分に配合することができる硬化剤として具体的には、カルボン酸やスルホン酸等の有機酸およびその無水物、有機ヒドロキシ化合物、シラノール基、アルコキシ基またはハロゲン基等の基を有する有機ケイ素化合物、一級または二級のアミノ化合物を例示することができ、またこれらを二種以上組み合わせて使用することもできる。また、(A)成分に配合することができる硬化促進剤として具体的には、三級アミン化合物、アルミニウムやジルコニウム等の有機金属化合物、ホスフィン等の有機リン化合物、異環型アミン化合物、ホウ素錯化合物、有機アンモニウム塩、有機スルホニウム塩、有機過酸化物等が例示される。また、(A)成分に配合することができる充填剤として具体的には、ガラス繊維、石棉、アルミナ繊維、アルミナとシリカを成分とするセラミック繊維、ボロン繊維、ジルコニア繊維、炭化ケイ素繊維、金属繊維、ポリエステル繊維、アラミド繊維、ナイロン繊維、フェノール繊維、天然の動物繊維等の繊維状充填剤、溶融シリカ、沈澱シリカ、ヒュードシリカ、焼成シリカ、酸化亜鉛、焼成クレイ、カーボンブラック、ガラスビーズ、アルミナ、タルク、炭酸カルシウム、クレイ、水酸化アルミニウム、硫酸バリウム、二酸化チタン、窒化アルミニウム、炭化ケイ素、酸化マグネシウム、酸化ベリリウム、カオリン、雲母、ジルコニア等の粉粒体状充填剤およびこれらの混合物が例示される。

【0012】 (B)オルガノポリシロキサンは、本発明の硬化性樹脂組成物の流動性を向上させ、またこれを硬化して得られた硬化樹脂の可撓性を向上させ、かつ金属等の被着体に対する接着性を向上させるための成分であり、一般式：

【化3】



で表されるオルガノポリシロキサンである。上式中、R

は炭素数5以下の低級アルキル基またはフェニル基であり、炭素数5以下の低級アルキル基として具体的に、メチル基、エチル基、プロピル基、ブチル基、ペンチル基が例示される。また、上式中、R<sup>1</sup>は炭素数5以下の低級アルキル基、フェニル基および水素原子からなる群から選択される基であり、R<sup>1</sup>の炭素数5以下の低級アルキル基として具体的には、メチル基、エチル基、プロピル基、ブチル基、ペンチル基が例示される。また、上式中、R<sup>1</sup>はエポキシ基含有有機基、アルコキシシリルアルキル基および炭素数6以上のアルキル基からなる群から選択される基であり、R<sup>1</sup>のエポキシ基含有有機基として具体的には、2-グリシドキシエチル基、3-グリシドキシプロピル基、4-グリシドキシブチル基、5-グリシドキシペンチル基、2-(3,4-エポキシシクロヘキシル)エチル基、3-(3,4-エポキシシクロヘキシル)プロピル基、4-(3,4-エポキシシクロヘキシル)ブチル基が例示され、R<sup>1</sup>のアルコキシシリルアルキル基として具体的には、トリメトキシシリルエチル基、トリメトキシシリルプロピル基、トリメトキシシリルブチル基、トリメトキシシリルペンチル基、トリエトキシシリルエチル基、トリエトキシシリルプロピル基、トリエトキシシリルブチル基、メチルジメトキシシリルエチル基、メチルジメトキシシリルプロピル基、ジメチルメトキシシリルエチル基、ジメチルメトキシシリルプロピル基が例示され、R<sup>1</sup>の炭素数6以上のアルキル基として具体的には、ヘキシル基、ヘプチル基、オクチル基、ノルシル基、デシル基、ウンデシル基、ドデシル基、トリデシル基、テトラデシル基、ペンタデシル基、ヘキサデシル基、ヘプタデシル基、オクタデシル基が例示され、n-ヘキシル基、n-ヘプチル基、n-オクチル基、n-ノルシル基、n-デシル基、n-ウンデシル基、n-ドデシル基、n-トリデシル基、n-テトラデシル基、n-ペンタデシル基、n-ヘキサデシル基、n-ヘプタデシル基、n-オクタデシル基が好ましい。(B)成分において、R<sup>1</sup>のアルキル基は炭素数が6以上であることが必要であり、その上限は特に限定されないが、これを(A)成分に配合した場合、(A)成分と(B)成分との相溶性が良好であり、得られる硬化樹脂組成物を硬化後の樹脂の機械性および接着性が良好であることから、R<sup>1</sup>のアルキル基の炭素数は6~30の範囲であることが好ましい。

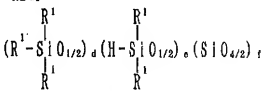
【0013】また、上式中、aはエポキシ基含有有機基、アルコキシシリルアルキル基または炭素数6以上のアルキル基を有しない官能性シロキサン単位(M単位)の数を示す0または正数であり、bはエポキシ基含有有機基、アルコキシシリルアルキル基または炭素数6以上のアルキル基を有する官能性シロキサン単位(M単位)の数を示す正数であり、cは四官能性シロキサン単位(Q単位)の数を示す正数であり、それぞれの比、a/cは0~4の範囲の数であり、b/cは0.05~

4の範囲の数であり、かつ(a+b)/cは0.2~2~4の範囲の数である。これは、四官能性シロキサン単位(Q単位)1個に対して、一官能性シロキサン単位(M単位)4個をこえることはできず、一官能性シロキサン単位(M単位)が0.2個未満であると、(A)成分と(B)成分の相溶性が低下するためである。また、本発明の硬化性樹脂組成物において、(A)成分と(B)成分の相溶性が優れるためには、(B)成分中のエポキシ基含有有機基、アルコキシシリルアルキル基または炭素数6以上のアルキル基を有する一官能性シロキサン単位(M単位)は、四官能性シロキサン単位(Q単位)1個に対して少なくとも0.05個であることが必要であるからである。(B)成分は室温で液状または固體状であり、その分子量は特に限定されないが、(A)成分との相溶性が良好であることから、500~5000, 000の範囲であることが好ましい。

【0014】本発明の硬化性樹脂組成物において、(B)成分は、アルコキシシリルアルキル基と炭素数6以上のアルキル基とを有しているため、(A)成分の樹脂マトリックス中に取り込まれることにより、得られた硬化樹脂の機械性が向上し、また(B)成分がSiO<sub>2</sub>単位(Q単位)からなるので、機械性および接着性に優れるという利点を有する。

【0015】上記(B)成分は、例えば、ヒドロシリル化反応用触媒の存在下、一般式：

【化4】



〔式中、R<sup>1</sup>は炭素数5以下の低級アルキル基またはフェニル基である。また、dは0または正数であり、eは正数であり、fは正数であり、d/fは0~4の数であり、e/fは0.05~4の数であり、かつ(d+e)/fは0.2~4の数である。〕で表されるオルガノシリロキサンにアルコキシシリルアルケンと炭素数6以上のアルケンと必要に応じてエポキシ基および脂肪族不飽和結合を有する有機化合物を付加反応させることにより調製することができる。

【0016】本発明の硬化性樹脂組成物において、(B)成分の配合量は、(A)成分100重量部に対して0.1~500重量部であり、好ましくは0.5~100重量部である。これは、(B)成分の配合量が、(A)成分100重量部に対して0.1重量部未満であると、得られた硬化樹脂の機械性が向上しないためであり、またこれが500重量部をこえると、得られた硬化樹脂の機械的強度が著しく低下するためである。

【0017】本発明の硬化性樹脂組成物は、(A)成分と

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(B)成分を均一に混合することにより調製することができ、(A)成分と(B)成分を混合する方法は特に限定されず、具体的には、(A)成分に直接(B)成分を配合する方法、(A)成分調製時に(B)成分を配合し、ブレミックスした後、(A)成分に充填剤等の添加剤を配合する方法、(B)成分に(A)成分に配合する各種の添加剤を順次配合する方法が例示される。(A)成分と(B)成分を混合する混合装置としては、特に限定がなく、(A)成分または(B)成分が液状、固体状、粉状等の種々の形態により混合装置は選択されるが、具体的には、一軸または二軸の連続混合機、二本ローラー、ロスミキサー、ニーダーミキサーが例示される。

【0018】本発明の硬化性樹脂組成物は、硬化前には流動性が優れるので、トランスファーモールド、インジェクションモールド、ポッティング、キャスティング、粉体塗装、浸漬塗布、滴下等の方法により使用することができる。また、本発明の硬化性樹脂組成物は、硬化後は可塑性および接着性に優れた硬化樹脂になるので、電気・電子素子を封止するための硬化性樹脂組成物、接着剤等に使用することができる。

【0019】

【実施例】本発明の硬化性樹脂組成物を実施例により詳細に説明する。なお、実施例中、粘度の値は25℃において測定した値であり、硬化性樹脂組成物および硬化樹脂の諸特性は下記の方法により測定した。

【0020】○スパイラルフロー：EMMI規格に準じた方法により測定した。

○成形収縮率：JIS-K-6911に準じた方法により測定した。

○熱膨張率：5mm×5mm×1.6mmに成形した硬化樹脂を熱膨張計（真空理工社製DLE-7000）を使用して測定した。熱膨張率の値は、室温からガラス転移点までの値である。

○ガラス転移点(Tg)：熱膨張率測定により測定した。

○曲げ弾性率：JIS-K-6911に準じた方法により測定した。

○吸水率：2インチ×0.5インチ×0.2mm

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\*5インチに成形した硬化樹脂を温度121℃、湿度100%にして20時間加湿した後、その硬化樹脂の重量増加を測定することにより求めた。

○バリ：深さ20μmの溝を使用して、バリ長さを測定した。

○接着性：硬化性樹脂組成物を42アロイ板および銅板に挟み、これを硬化させた後、硬化樹脂を剥す際の接着性を○（良好）、×（不良）により判断した。

10 ○耐熱衝撃性：チップサイズ36mm<sup>2</sup>、パッケージ厚さ2.0mmの樹脂封止半導体素子20個を成形し、これを-196℃→+150℃で1分間のサイクルでヒートサイクル試験を行い、150サイクル後に封止樹脂表面を実体顕微鏡で観察して、表面にクラックの入った成形品の個数が5個以下である場合を○、6～10個である場合を△、11個以上である場合を×とした。

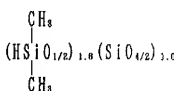
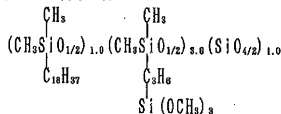
○半田耐熱性：チップサイズ36mm<sup>2</sup>、パッケージ厚さ2.0mmの樹脂封止半導体素子20個を成形し、これを85℃で85%RH条件下にて72時間放置後、直ちに240℃の半田浴に1時間浸漬し、封止樹脂表面を実体顕微鏡で観察した。表面にクラックの入った成形品の個数が5個以下である場合を○、6～10個である場合を△、11個以上である場合を×とした。

【0021】

【参考例1】攪拌装置、還流冷却管および温度計付きの四つ口フラスコに、テトラキス（ジメチルシロキシ）シランをトルエン中でアルトリメトキシシランと1-オクタデンを塩化白金酸の存在下に反応させて、黄褐色透明なオルガノポリシロキサンを調製した。このオルガノポリシロキサンの粘度は2.4センチポイズであり、屈折率は1.4358であった。このオルガノポリシロキサンを<sup>1</sup>H-核磁気共鳴スペクトル分析（以下、NMR）、<sup>13</sup>C-NMRおよび<sup>29</sup>Si-NMRにより分析したところ、次の構造式で表されることが確認された。

【0022】

【化5】



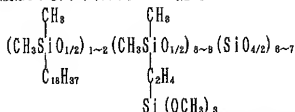
【0023】

【参考例2】攪拌装置、還流冷却管および温度計付きの四つ口フラスコに、式：

【化6】

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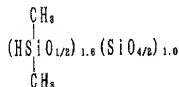
で表されるオルガノポリシロキサン（粘度4.6センチポイズ、ケイ素原子結合水素原子の含有量0.92重量%）をトルエン中で、1-オクタデセンとビニルトリメトキシシランを塩化白金酸触媒の存在下で反応させて、無色透明なオルガノポリシロキサンを調製した。このオルガノポリシロキサンの粘度は9.7センチポイズであ \*



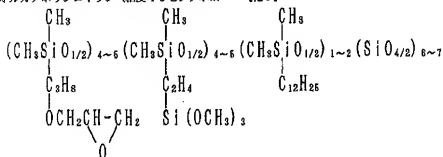
【0025】

【参考例3】攪拌装置、還流冷却管および温度計付きの四つフラスコに、式：

【化8】



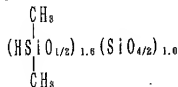
で表されるオルガノポリシロキサン（粘度4.6センチポイズ、



【0027】

【参考例4】攪拌装置、還流冷却管および温度計付き四つフラスコに、式：

【化10】



で表されるオルガノポリシロキサン（粘度4.6センチポ

10

イズ、屈折率は1.4386であった。このオルガノポリシロキサンを<sup>1</sup>H-NMR、<sup>13</sup>C-NMRおよび<sup>29</sup>Si-NMRにより分析したところ、次の構造式で表されることが確認された。

【0024】

【化7】

※イズ、ケイ素原子結合水素原子の含有量0.92重量%）をトルエン中で、1-ドデセン、ビニルトリメトキシシランとアリルグリシジルエーテルを塩化白金酸触媒の存在下で反応させて、無色透明なオルガノポリシロキサンを調製した。このオルガノポリシロキサンの粘度は1.42センチポイズであり、屈折率は1.4475であった。このオルガノポリシロキサンを<sup>1</sup>H-NMR、<sup>13</sup>C-NMRおよび<sup>29</sup>Si-NMRにより分析したところ、次の構造式で表されることが確認された。

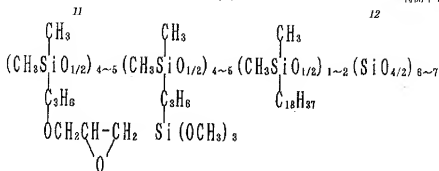
【0026】

【化9】

イズ、ケイ素原子結合水素原子の含有量0.92重量%）をトルエン中で、1-オクタデセンとビニルトリメトキシシランを塩化白金酸の存在下で反応させて、無色透明なオルガノポリシロキサンを調製した。このオルガノポリシロキサンの粘度は9.7センチポイズであり、屈折率は1.4386であった。このオルガノポリシロキサンを<sup>1</sup>H-NMR、<sup>13</sup>C-NMRおよび<sup>29</sup>Si-NMRにより分析したところ、次の構造式で表されることが確認された。

【0028】

【化11】



{0029}

〔実施例 1〕 エポキシノボラック樹脂 (軟化点 80℃、水酸基当量 100) 100重量部、参考例 1 で調製したオキソノボラック系 8、9 重量部、溶剤メチルセリソル 18.5、7 重量部、ヘキサスチレンテトラミン 11、4 重量部、3-グリシドシロピロリドメチルセリソラン 1、0 重量部およびバルグナリウックス 2、9 重量部を均一に混合し、その 90℃での加熱ロールでさらに混練後冷却して本発明の硬化性樹脂組成物を調製した。次いで、これを粉砕し、175℃、7.0 kg/cm<sup>2</sup> の条件下で 3 分間トランスフュム成形した。その後、硬化樹脂を 150℃で 2 時間かけてポストキュアした。得られた硬化樹脂の特性を表 1 に示した。

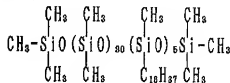
【0030】

【比較例１】実施例１において、参考例１で調製したオルガノポリシロキサンの代わりに下式で表されるオルガノポリシロキサンを使用した以外は実施例１と同様にして硬化性樹脂組成物を調製した。これを実施例１と同様\*

\*にして硬化させた。得られた硬化樹脂の諸特性を表1に示した。

[0031]

【化12】



[0 0 3 2]

【比較例2】実施例1において、参考例1で調製したオルガノポリシロキサンを使用しない以外は実施例1と同様にして硬化性樹脂組成物を調製した。これを実施例1と同様にして硬化させた。得られた硬化樹脂の諸特性を表1に示した。

**[0033]**

【表 1】

測 定 項 目	本発明	比 較 例	
	実施例 1	比較例 1	比較例 2
スパイラルフロー (むね)	89	84	81
成形収縮率 (%)	0.23	0.20	0.31
熱膨張率 ( $\times 10^{-5}/^{\circ}\text{C}$ )	1.19	1.05	1.50
ガラス転移点 ( $^{\circ}\text{C}$ )	161	138	156
曲げ弾性率 ( $\text{kgf}/\text{mm}^2$ )	1200	1260	1350
吸水率 (%)	0.39	0.56	0.51

[0 0 3 4]

実施例21  $\text{CH}_3\text{SiO}_{2.72}$  単位 40モル%,  $\text{C}_6\text{H}_5$  ( $\text{CH}_3$ )  $\text{SiO}_{2.72}$  単位 40モル%,  $\text{C}_6\text{H}_5\text{SiO}_{2.72}$  単位 40モル%および  $(\text{C}_6\text{H}_5)_2\text{SiO}_{2.72}$  単位 10モル%からなり、ケイ素原子結合水酸基を5重量%含有するシリコーン樹脂(50重量部)とゾルノールブロックエポキシ樹脂(軟化点80℃、エポキシ当量220)50重量部からなるシリコーン-エポキシ樹脂100重量部、参照例2で調製したオルガノシリロキサセラム0.重量部、溶剤系粉体28.4、6重量部、アルミニウム

アセチルアセトネート 3、5重量部、3-グリシドキシプロピルトリメトキシシラン1、0重量部およびカルナバウワックス 3、8重量部とを均一に混合し、これを90℃の加熱ロールでさらに熔融後冷却して本発明の硬化性樹脂組成物を調製した。次いで、これを粉砕し、175℃、70 kg/cm<sup>2</sup>の条件下で2分間トランスファモールド成形した。その後、この硬化樹脂を180℃で12時間かけてポストキュアした。得られた硬化樹脂の諸特性を表2に示した。

[0035]



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【実施例3】実施例2において、参考例2で調製したオルガノポリシロキサン10の代わりに参考例3で調製したオルガノポリシロキサンを使用した以外は実施例2と同様にして、硬化性樹脂組成物を調製した。これを実施例2と同様にして硬化させた。得られた硬化樹脂の諸特性を表2に示した。

【0036】

【実施例4】実施例2において、参考例2で調製したオルガノポリシロキサン10の代わりに参考例4で調製したオルガノポリシロキサンを使用した以外は実施例2と同様にして、硬化性樹脂組成物を調製した。これを実施例2※

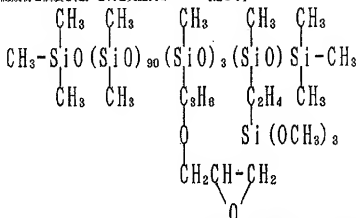
と同様にして硬化させた。得られた硬化樹脂の諸特性を表2に示した。

【0037】

【比較例3】実施例2において、参考例2で調製したオルガノポリシロキサン10の代わりに下記の構造式で表されるオルガノポリシロキサンを使用した以外は実施例2と同様にして硬化性樹脂組成物を調製した。これを実施例2と同様にして硬化させた。得られた硬化樹脂の諸特性を表2に示した。

【0038】

【化13】



【0039】

【比較例4】実施例2において、参考例2で調製したオルガノポリシロキサンを添加しない以外は実施例2と同様にして硬化性樹脂組成物を調製した。これを実施例2※

と同様にして硬化させた。得られた硬化樹脂の諸特性を表2に示した。

【0040】

【表2】

測定項目	本 発 明			比 較 例	
	実施例2	実施例3	実施例4	比較例3	比較例4
スバイタルプルー (化付)	45	44	42	40	85
熱膨張率 ( $\times 10^{-5}/^{\circ}\text{C}$ )	2.26	2.18	2.15	2.90	2.75
曲げ弾性率 ( $\text{kgf}/\text{mm}^2$ )	1110	1090	1150	1250	1520
吸水率 (%)	0.40	0.39	0.38	0.56	0.47
バリ (mm)	3	5	4	15	4
接着性	○	○	○	△	×
耐熱衝撃性	○	○	○	△	×
半田耐熱性	○	○	○	×	×

【0041】

【実施例5】ビスマレイミド-トリアジン型の熱硬化性ポリイミド樹脂10重量部、参考例3で調製したオルガノポリシロキサン12重量部、溶融石英粉末185、7重量部、カルバウワックス2、9重量部および安息香酸アルミニウム0、9重量部とを均一に混合し、これ

を90℃の加熱ロールでさらに混練後冷却して本発明の硬化性樹脂組成物を調製した。次いで、これを粉碎して、220℃、70kg/cm<sup>2</sup>の条件下で4分間トランスファモールド成形した。その後、この硬化樹脂を230℃で3時間かけてポストキュアした。得られた硬化樹脂の諸特性を表3に示した。

【0042】

【比較例5】実施例5において、参考例3で調製したオルガノポリシロキサンを使用しない以外は実施例5と同様にして硬化性樹脂組成物を調製した。これを実施例5と同様に硬化させた。この硬化樹脂の諸特性を表3に示した。

【0043】

【表3】

測定項目	本発明	比較例
	実施例5	比較例5
スパイラルフロー (1/f)	53	44
曲げ弾性率 (kgf/cm <sup>2</sup> )	960	1220
接着性	○	×

【0044】

【実施例6】オルソクレゾールノボラックエポキシ樹脂（軟化点80℃、エポキシ当量220）75重量部、熔融シリカ260重量部、カルナバウワックス1重量部、フェノールノボラック樹脂35重量部、トリフェニルフォスフィン0.6重量部、参考例4で調製したオルガノポリシロキサン13重量部および3-グリシドキシプロピルトリメトキシシラン1.0重量部を均一に混合し、これを90℃の加熱ロールでさらに混練後冷却して本発明の硬化性樹脂組成物を調製した。次いで、これを粉砕し、150℃、7.0 kg/cm<sup>2</sup>の条件下で3分間トランスファモールド成形した。その後、この硬化樹脂を180℃で4時間かけてポストキュアした。得られた硬化樹脂の諸特性を表4に示した。

【0045】

【比較例6】実施例6において、参考例4で調製したオルガノポリシロキサンを使用しない以外は実施例6と同様にして硬化性樹脂組成物を調製した。これを実施例6と同様に硬化させた。得られた硬化樹脂の諸特性を表4に示した。

【0046】

【表4】

測定項目	本発明		比較例
	実施例7	実施例8	比較例7
接着強度 (kgf/cm <sup>2</sup> )	6.5	6.2	5.0

測定項目	本発明	比較例
	実施例6	比較例6
スパイラルフロー (1/f)	75	55
成形収縮率 (%)	0.35	0.40
熱膨張率 (×10 <sup>-5</sup> /℃)	2.52	2.71
曲げ弾性率 (kgf/cm <sup>2</sup> )	1120	1420
吸水率 (%)	0.45	0.55
バリ (mm)	2	2
接着性	○	×
耐熱衝撃性	○	×
半田耐熱性	○	×

【0047】

【実施例7】3, 4-エポキシシクロヘキシル-3, 4-エポキシシクロヘキサンカルボキシレート100重量部、3または4-メチルヘキサハイドロフタリックアンハイドライド120.5重量部、オクチル酸錫1.4重量部および参考例2で調製したオルガノポリシロキサン24重量部を均一に混合して本発明の硬化性樹脂組成物を調製した。これを、1mm厚のニッケル板に挟み、210℃、2時間で加熱後、さらに150℃で3時間加熱して、樹脂を硬化させた。硬化樹脂のニッケル板に対する接着強度を測定した。この結果を表5に示した。

【0048】

【実施例8】実施例7において、参考例2で調製したオルガノポリシロキサンの代わりに参考例4で調製したオルガノポリシロキサンを使用しない以外は実施例7と同様にして硬化性樹脂組成物を調製した。これを実施例7と同様に硬化させた。得られた硬化樹脂のニッケル板に対する接着強度を測定した。この結果を表5に示した。

【0049】

【比較例7】実施例7において、参考例2で調製したオルガノポリシロキサンを使用しない以外は実施例7と同様にして硬化性樹脂組成物を調製した。これを実施例7と同様に硬化させた。得られた硬化樹脂のニッケル板に対する接着強度を測定した。この結果を表5に示した。

【0050】

【表5】

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【0051】

【発明の効果】本発明の硬化性樹脂組成物は、(B)成分として、一分子中にアルコキシシリルアルキル基と炭素数6以上のアルキル基とを少なくとも1個づつ有するオ

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ルガノポリシロキサンを配合しているので、硬化前は流動性が優れ、硬化後には可換性および接着性が優れた硬化樹脂を得ることができるという特徴を有する。

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